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# RESEARCH IN MATERIALS SCIENCE AND ENGINEERING

Massachusetts Institute of Technology
Cambridge, Massachusetts

April 1968

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# ANNUAL REPORT 1967-68

# RESEARCH IN MATERIALS SCIENCE AND ENGINEERING

MASSACHUSETTS INSTITUTE OF TECHNOLOGY



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DEPARTMENT OF DEFENSE

*Advanced Research Projects Agency:*

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NATIONAL SCIENCE FOUNDATION

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1 R01 GM-15310-01BBCB (Lord); DEO2384-02 (Cahn); HE-08598 (Merrill, K. A. Smith, Gilliland).

DEPARTMENT OF COMMERCE

C-85-65 Northeast Corridor Transportation Project (Thornton, Navon, McGarry, Williamson, Moavenzadeh); CST-1170 (Backer, Yannas).

NATIONAL BUREAU OF STANDARDS

CST-280 (Elliott).

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ANNUAL REPORT 1967-68

RESEARCH IN MATERIALS
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OF TECHNOLOGY

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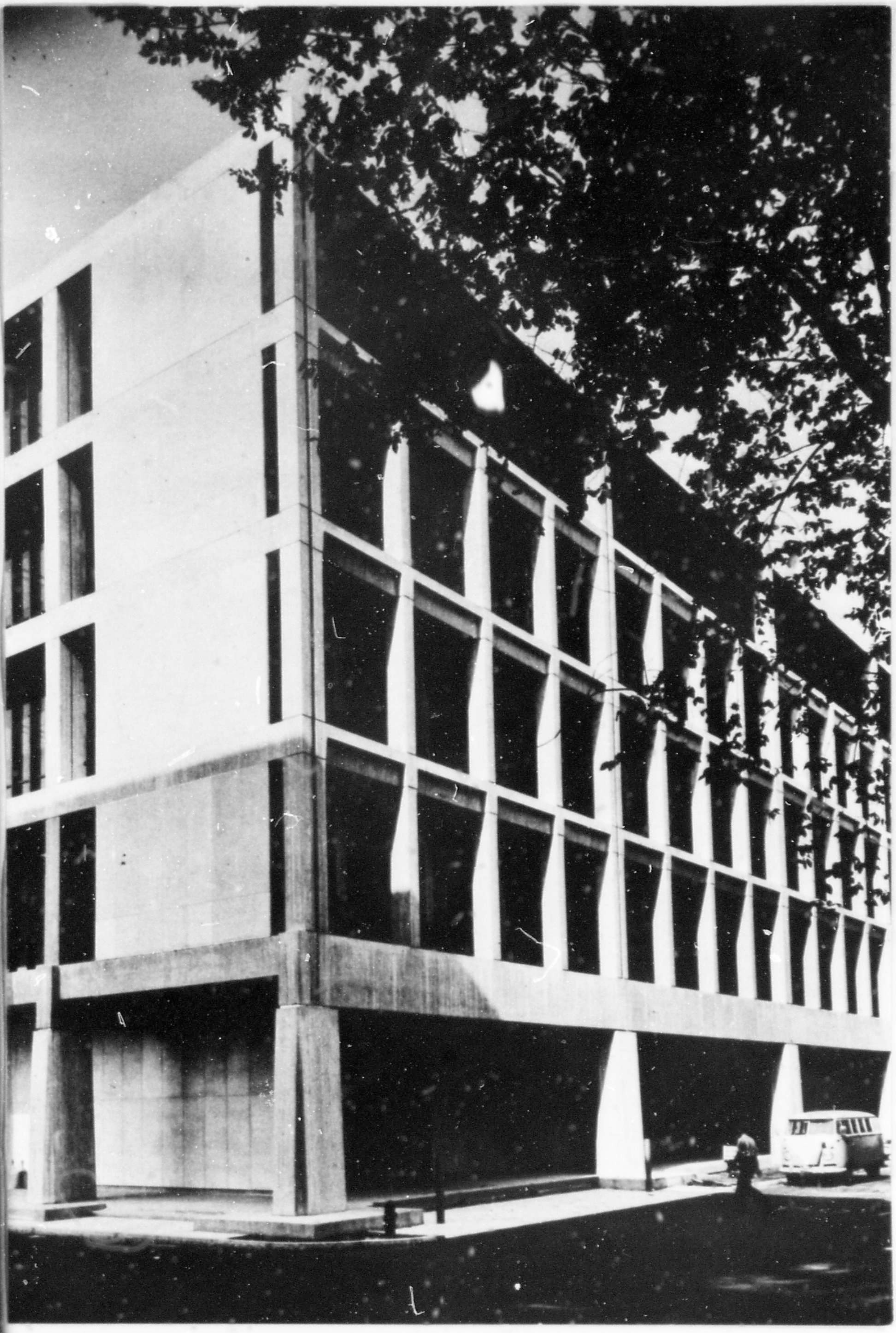
APRIL, 1968



OFFICE OF THE PROVOST

CAMBRIDGE, MASSACHUSETTS 02139

This Annual Report on materials research and development activities at MIT, as well as related work in the Lincoln Laboratory, the Instrumentation Laboratory and the National Magnet Laboratory, brings together in one volume work of most of the faculty members and research groups interested in materials. It was prepared for the MIT community by the Center for Materials Science and Engineering and is intended to give a comprehensive view of such activities on the campus.

It is the aim of this report to provide both a general view of the research on materials at MIT and a sufficiently specific description of each research effort to be useful to the specialists.

Materials science and engineering activities are an important aspect of the teaching and research programs in many departments of the School of Engineering and the School of Science, including the Departments of Electrical Engineering, Mechanical Engineering, Metallurgy and Materials Science, Aeronautics and Astronautics, Naval Architecture and Marine Engineering, Civil Engineering and Chemical Engineering, the Departments of Chemistry, Biology, Physics and Geology and Geophysics so that this field represents one of the most extensive and all-pervading activities on the MIT campus. This, in fact, has always been the case but whereas in former times there was very little of common interest to draw various activities together, the advances in the fundamental understanding of the nature of matter have provided an underlying base upon which many of these activities now build. Each feeds the other to a much greater extent than ever before, and the activities of the departments now overlap to some extent, although with differences in motivation and emphasis as in the case, for example, in the field of electronic properties of materials where the Departments of Metallurgy and Materials Science, Electrical Engineering and Physics are deeply involved. This report attempts to reflect both the extensiveness of the materials science and engineering activities at MIT and the growing interrelationships among the areas.

JBWiesner

Jerome B. Wiesner, Provost
Massachusetts Institute of Technology

March 1968

## SURVEY

This is the seventh in the series of Annual Reports on Research in Materials Science and Engineering at the Massachusetts Institute of Technology to be issued on behalf of the Institute by the Center for Materials Science and Engineering. There are very few of the academic departments in the Schools of Science and Engineering that are not involved in some way in materials research and teaching. The Interdisciplinary Laboratory, which was built with funds made available jointly by MIT and the Advanced Research Projects Agency, although only accommodating a fraction of the total effort on materials research at MIT, provides an important addition to the available laboratory space and facilities of materials research. Its Central Facilities (see below) make possible research which could not otherwise, or at any rate with great difficulty, be carried out in an academic environment. It accommodates at the moment 51 professors and their students (about 190 graduate students) as well as about 22 post-doctoral research workers and visiting scientists. These are supported by a complement of engineering assistants, technicians, secretaries, etc. In addition a good deal of materials research is carried out in the Research Laboratory for Electronics (RLE) and in special laboratories such as the National Magnet Laboratory, the Instrumentation Laboratory and Lincoln Laboratory

The report deals with work on materials in all these laboratories and in the various Academic Departments. Individual programs can be identified together with their sponsorship in the acknowledgments included in the report and also from the list on the inside of the front cover.

We have followed fairly closely the arrangement of previous reports dividing the subject matter into a number of sections, as follows:

A. Chemical and Solid State Physics

B. Electric, Magnetic, and Optical Properties of Materials and Applications to Devices

C. Metallurgy and Materials Science

D. Materials Engineering

These sections deal mainly with work carried out in the Interdisciplinary Laboratory of the Center for Materials Science and

Engineering, in the Academic Departments and in the Research Laboratory of Electronics directed by Professor H. J. Zimmermann. Reports in each section identify the Department and/or Laboratory concerned. The work of the three other laboratories listed above is included in the following sections:

E. National Magnet Laboratory
(Director, Professor Benjamin Lax)

F. Instrumentation Laboratory
(Director, Professor C. Stark Draper)

G. Lincoln Laboratory
(Director, Dr. Milton U. Clauser)

The research program of the National Magnet Laboratory is mainly of a fundamental nature and the report covers a large portion of the work of this laboratory. For the Instrumentation Laboratory and the Lincoln Laboratory a much greater fraction of the work is of a more applied nature or is concerned with bridging the gap between pure research and application. There is, however, in both laboratories a good deal of basic research on the properties of materials and it is this that is included in the report.

There is a great deal of overlapping between the work in the Academic Departments and that in the special laboratories and this overlapping is likely to increase rather than diminish. It is part of the interdisciplinary climate that is pervading our research and teaching.

Central facilities for materials preparation and characterization, made possible through the ARPA Contract SD-90, are mainly installed and in operation in the interdisciplinary laboratory. Section H describes these facilities briefly and lists the staff associated with them.

The ARPA funds have enabled us to update these facilities from time to time and also to extend them, a recent addition being a Stereoscan electron microscope which is finding application in many areas of research.

One of the great advantages of a research center like MIT is that a great many existing facilities are also available. For example there is the high magnetic field facility in the National Magnet Laboratory. There is also the Spectroscopy Laboratory under the direction of Professor R. C. Lord of the Department of Chemistry which provides a wealth of spectroscopic experience as well as excellent facilities. Coolants for low temperature work are provided by the Cryogenic Laboratory in the Department of Mechanical Engineering under Professor J. L. Smith, Jr.

The Administrative Office of the Center for Materials Science and Engineering is located in the Vannevar Bush Building which houses the interdisciplinary laboratory. This office has been responsible for the issue of this report on behalf of the Institute. We will be distributing copies to those who returned the card enclosed with last year's copy indicating their continued interest in the report, and to those who have made recent requests for a copy. Requests for copies of the report and requests to be placed on the mailing list for future issues should be addressed to Mr. Elwood W. Schafer, Administrative Officer of the Center for Materials Science and Engineering, Room 13-2145, MIT, Cambridge, Massachusetts 02139.

In conclusion I wish again to thank all my colleagues at MIT who have contributed to this report for their help in making it so comprehensive; also Mr. E. W. Schafer and his office staff and a number of our secretaries who have undertaken the many detailed tasks involved in assembly and preparation of the report for publication.

R. A. Smith
Director, Center for Materials
Science and Engineering

March 1968

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# SECTION A

# CHEMICAL AND SOLID-STATE PHYSICS

## I. SOLID STATE AND MOLECULAR THEORY GROUP

### Personnel

Professor J. C. Slater, Institute Professor, Emeritus, Physics
Professor G. F. Koster, Professor, Physics
Professor P. D. DeCicco, Assistant Professor, Physics
E. Lafon, Visiting Scientist, Physics
J. W. Gadzuk, Instructor, Physics
R. Gilmore, Instructor, Physics
D. S. Becker, Research Assistant, Physics
W. E. Rudge, Research Assistant, Physics
D. Klingspon, Graduate Student, Physics
D. Koelling, Graduate Student, Physics
B. Mayes, Graduate Student, Physics
Josephine Shea, Secretary, Physics

### Personnel who have left during the period

Dr. A. J. Freeman, Associate Director, National Magnet Laboratory (Now Head of the Physics Dept., Northwestern University)
Dr. A. Kitz, Visiting Scientist, Physics (Now at the University of Hamburg, Germany)
J. F. Kenney, Research Assistant, Physics (Now at the University of Edinburgh, Scotland)
J. Sokoloff, Graduate Student, Physics (Now at Brookhaven National Laboratory)

### Degrees Granted

R. Gilmore, Ph.D., Physics, January 1967
J. Kenney, Ph.D., Physics, June 1967
J. Sokoloff, Ph.D., Physics, September 1967

### Sponsorship

Office of Naval Research, Nonr-1841(34), DSR 70280
National Science Foundation, NSF-GP-3241, DSR 75251

National Science Foundation, NSF-GP-7677, DSR 70607

## Research Report

As in preceding Annual Reports, we indicate the fields of interest of the members of the group by indicating the titles of the contributions to the four Quarterly Progress Reports issued during the year, namely Reports Nos. 63, 64, 65, and 66, issued on January 15, April 15, July 15, and October 15, 1967, respectively.

## Contents of Quarterly Progress Reports Nos. 63, 64, 65, and 66:


P. DeCicco and A. Kitz, Calculation of Charge and Spin Densities for Iron, 63.

P. DeCicco, A Note on the $\ell$-Convergence of the APW Method, 65.

J. W. Gadzuk, Impurity Screening in an Inhomogeneous Electron Gas I. General Formalism; Simple RPA Screening, 64.

J. W. Gadzuk, Impurity Screening in an Inhomogeneous Electron Gas II. Mass Operator Formalism: Point Impurity in the Surface Region, 65.

J. W. Gadzuk, Field Theory of an Interacting Electron Gas in a Periodic Potential, 65.

J. W. Gadzuk, The Effects of Screened Exchange and Correlation on the Surface Potential of an Electron Gas, 66.

R. Gilmore, Branching Diagrams, 64.

R. Gilmore, The Quantum Origin and Significance of Maxwell's Equations, 65.

R. Gilmore, Stellar Maser, 66.

R. Gilmore, Darwin Again, 66.

J. F. Kenney, The A. P. W. Eigenfunctions for the Deformed Lattice, 63.

J. F. Kenney, Energy Bands in Rubidium and Cesium, 66.

D. Koelling, A Preliminary Note on Symmetrizing the Relativisitc APW Calculations, 63.

D. Koelling, A Crystal Potential for Grey Tin, 64.

D. Koelling, Double Space Group Representations for the Diamond ($O_h^7$) and White Tin ($D_{4h}^{19}$), 66.

J. C. Slater, Lectures on the Energy Band Theory of Magnetism, 65.

J. C. Slater, Exchange in Magnetic Atoms, 65.

J. Sokoloff, Electronic States of Magnetic Impurities in Nonmagnetic Metals, 63.

J. Sokoloff, Electronic States of Magnetic Impurities in Nonmagnetic Metals, 64.

J. Sokoloff, Electronic States of Magnetic Impurities in Nonmagnetic Metals II, 65.

J. Sokoloff, Some Primitive Thoughts on Localized Moment Structure in Metals, 65.

## Theses

R. Gilmore, "Theory of Representations Applied to Relativistic Wave Equations," Ph. D. Thesis, Department of Physics, January 1967.

J. Kenney, "Electron-Phonon Interaction in Normal Metals," Ph. D. Thesis, Department of Physics, June 1967.

J. Sokoloff, "Electronic States of Magnetic Impurities in Nonmagnetic Metals," Ph. D. Thesis, Department of Physics, September 1967.

## Publications


P. DeCicco, "Self-Consistent Energy Bands and Cohesive Energy of Potassium Chloride", Phys. Rev. 153, 931-938 (1967).

J. W. Gadzuk, "Single-Phonon Energy Transfer between Molecular Beams and Solid Surfaces", Phys. Rev. 153, 759 (1967).

J. W. Gadzuk, "Nodal Hydrogenic Wave Functions of Impurities on Bounded-Electron Gas Surfaces", Phys. Rev. 154, 622 (1967).

J. W. Gadzuk, "Theory of Atom-Metal Interactions I. Alkali Atom Adsorption", Surface Sci. 6, 133 (1967).

J. W. Gadzuk, "Theory of Atom-Metal Interaction II. One-Electron Transition Matrix Elements", Surface Sci. 6, 159 (1967).

H. Statz, C. L. Tang, and G. F. Koster, "Transition Probabilities between Laser States in Carbon Dioxide", Am. Inst. of Phys. 37, 4278 (1966).

J. C. Slater, "The Current State of Solid-State and Molecular Theory", Inter. J. Quantum Chem. 1, 37 (1967).

J. C. Slater, "Introduction to the Theory of Ferroelectricity", E. Weller, Editor, (1967).

J. C. Slater, "Insulators, Semiconductors, and Metals", Vol. 3, Quantum Theory of Molecules and Solids, McGraw Hill Publishing Co., New York (1967).

J. Sokoloff, "Electronic Structure of Magnetic Impurities in Copper", Phys. Rev. 161, 540 (1967).

# II. NON-EQUILIBRIUM QUANTUM STATISTICAL MECHANICS

## Personnel

Professor M. Scully, Assistant Professor, Physics
Dr. D. Kim, DSR Staff, Center for Materials Science and Engineering
I. Asher, Research Assistant, Physics
R. Lang, Research Assistant, Physics
F. Hopf, Graduate Fellow, Physics (Yale University)
P. Lee, Graduate Fellow, Physics
J. Blinkship, Senior Student, Physics

## Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75105

## Research Report

### 1.0 Quantum Theory of an Optical Maser

Personnel: Professor M. Scully; Dr. D. Kim

The quantum theory of an optical maser, as developed in collaboration with W. E. Lamb provides a basis for answering any physically sensible question about a laser. In three recent papers we have developed the general theory and extended the analysis to include a proper quantum mechanical treatment of a spectrum analyzer and photodetector. The effects of atomic motion on the spectrum and statistics of a laser have been determined and prepared for publication.

### 2.0 Acousto-Electric Effect

Personnel: Professor M. Scully; I. Asher

The generation of a coherent phonon beam (sound wave) has been achieved by means of acousto-electric amplification. We have developed a detailed theoretical description of this effect. The scattering of light from such a coherent phonon excitation is under investigation.

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## 3.0 Coherence in Atomic Processes

Personnel: Professor M. Scully; F. Hopf

The importance of coherence in atomic systems is dramatically illustrated in the recent photon-echo and self-induced transparancy experiments. We have analyzed the problem of observing a photon echo in a gaseous medium. In other work we have considered the amplification of an ultra-short pulse electromagnetic radiation by a medium of two level atoms characterized by a phase memory time $T_2$ and having a spread in atomic frequencies, i.e. the medium is inhomogeniously broadened. We obtain the electric field at the output of the amplifier for general initial conditions. Connection is made with the work of Hahn and McCall who consider an inhomogeneously broadened attenuating medium. We believe this analysis characterizes a laser amplifier with a realism heretofore unattained.

## 4.0 Superfluid Physics

Personnel: Professor M. Scully; R. Lang; P. Lee

Investigation is being initiated in the field of superconductivity and liquid helium II. One of the outstanding properties of superconducting systems is their coherence. The radiation emitted by the usual tunnel junction device is a manifestation of this coherence. In as much as this radiation is now used to provide a value for the line structure constant $\alpha$ it is of interest to investigate the noise limitation of such a device. Progress is being made on this problem.

## Publications

M. O. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser", I. General Theory, Phys. Rev. 159, 208 (1967).

M. O. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser", II. Theory of a Spectrometer, Phys. Rev. (To be published)

M. O. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser", III. Photoelectron Counting Statistics, Phys. Rev. (To be published)

M. O. Scully, "Quantum Theory of a Laser, A Problem in Non-Equilibrium Statistical Mechanics", (1967), Enrico Fermi Summer School

Lectures, Acad. Press (To be published)

W. E. Lamb and M. O. Scully, "The Photoelectric Effect without Photons", Kastler Festschift (1967).

M. O. Scully, M. J. Stephen, and D. C. Burnham, "Photon Echo in Gaseous Media", submitted to Phys. Rev. Letters.

D. M. Kim, M. O. Scully, and W. E. Lamb, Jr., "Effects on Atomic Motion on the Spectrum and Statistics of a Laser", submitted for publication.

## III. CRYSTAL AND SURFACE STRUCTURE INVESTIGATIONS OF METALS, ZEOLITES, AND OTHER SUBSTANCES BY X-RAY, NEUTRON, AND ELECTRON DIFFRACTION

### Personnel

Professor D. P. Shoemaker, Professor, Chemistry
Dr. Clara B. Shoemaker, Research Associate, Chemistry
Dr. G. R. Eulenberger, Research Associate, Chemistry
M. A. Taylor, Research Assistant, Chemistry
J. G. Keil, Research Assistant, Chemistry
P. C. Manor, Research Assistant, Chemistry
Joan M. Flaherty, Secretary, Chemistry

### Sponsorship

Army Research Office (Durham), DA-31-124-ARO(D)-358, DSR 74966
Advanced Research Projects Agency, SD-90, DSR 78883
National Science Foundation, GP-4977, DSR 76025
Humble Oil and Refining Co., DSR 78996

### Research Report

#### 1.0 X-ray and Neutron Diffraction Studies of Metals and Alloys

Sponsorship: Army Research Office, Durham

Work on the crystal structure of the I phase (V-Ni-Si), which was started several years ago, was concluded with the publication of the cell dimensions and the indexed powder pattern.

$$a_o = 13.403(6),\ b_o = 23.336(15),\ c_o = 9.129(6)\ \text{A}^o$$
$$\beta = 99.11(6)^o$$

The space group is Cc (or C 2/c) and the density indicates that there may be an many as 240 atoms per unit cell. The structure seems to be related to the $\mu$ phase, but represents a considerable distortion of it. The quality of the crystals makes further work on a structure of this complexity unfeasible. It was demonstrated that the S phase, discovered by Kuzma and Hladyshevskii in the Mn-Co-Si system is probably isostructural with the I phase.

Work on the D phase is continuing with the search for better single crystals in the quaternary Mn-V-Fe-Si system.

The study of the K phase, discovered by K. P. Gupta in the Fe-Mn-Si system, was started and has indicated so far that a structural relationship between this phase and the $\sigma$ phase exists.

Attempts to obtain large single crystals of iron-and cobalt-containing sigma phases for neutron magnetic scattering work has so far proven unsuccessful.

## 2.0 Fundamental Studies in the Field of Aluminas, Molecular Sieves, and Related Materials

Sponsorship: Humble Oil and Refining Company

Work is continuing on our studies of hydrogen positions in hydrogen-form faujasite, with new neutron diffraction data from H and D forms, and on the structure of the new body-centered-cubic zeolite.

## 3.0 Low-Energy Electron Diffraction (LEED)

Sponsorship: National Science Foundation, Advanced Research Projects Agency

The rebuilding of our apparatus for low-temperature work on surfaces produced by cleavage has been completed. Work on physical absorption of noble gases on vacuum-cleaved zinc (0001) surfaces will soon commence.

Extensive intensity data have been collected on the Varian unit for (00) scattering, as a function of incident energy, from (110) CdTe, ZnTe, and ZnSe. The data are partially interpretable on the basis of Bragg peaks (shifted by inner potential) and step peaks (un-shifted) but other maxima have been observed (possibly resonance phenomena) still subject to interpretation. Both these data and photographic data for other reflections conform to expected symmetries.

## Publications

W. M. Meier and D. P. Shoemaker, "The Structure of a Bromine Sorption Complex in Synthetic Zeolite Sodium-A", Zeit, für Krist., 123, 5 (1966).

K. Seff and D. P. Shoemaker, "The Structures of Zeolite Sorption Complexes. I. The Structures of Dehydrated Zeolite 5a and its Iodine Sorption Complex", Acta Cryst., 22, 162 (1967).

G. R. Eulenberger, D. P. Shoemaker, and J. G. Keil, "The Crystal Structures of Hydrated and Dehydrated Synthetic Zeolites with Faujasite Aluminosilicate Frameworks. I. The Dehydrated Sodium, Potassium, and Silver Forms," J. Phys. Chem., 71, 1812 (1967).

C. B. Shoemaker and D. P. Shoemaker, "The Crystal Structure of the M Phase, Nb-Ni-Al", Acta Cryst., 23, 231 (1967).

C. B. Shoemaker and D. P. Shoemaker, "On the Structure of the I Phase (V-Ni-Si) and the S Phase (Mn-Co-Si)", Trans. A.I.M.E., 239, 937 (1967).

D. P. Shoemaker, and C. B. Shoemaker, "Sigma-Phase-Related Transition Metal Structures with Tetrahedral Interstices", Chapter in Pauling Festschrift (W. H. Freeman, in press for 1967 or 1968).

D. P. Shoemaker, "Optimization of Counting Times in Computer-Controlled X-ray and Neutron Single-Crystal Diffractometry", Acta Cryst. in press (1968).

D. P. Shoemaker and G. Bassi, "On Refinement of the Crystal Orientation Matrix and Lattice Constants with Diffractometer Data", submitted to Acta Cryst.

# IV. NEUTRON DIFFRACTION AND NEUTRON PHYSICS STUDIES

## Personnel

Professor C. G. Shull, Physics
Dr. R. Ciszewski, DSR Staff, Physics
Dr. W. Just, DSR Staff, Physics
Y. Ito, Research Assistant, Physics
R. Maglic, Research Assistant, Physics
C. S. Schneider, Research Assistant, Physics
A. C. Nunes, Research Assistant and Kennecott Copper Corporation Fellow, Physics
C. Stassis, Research Assistant, Physics
L. A. Schwarzkopf, Senior Thesis Student, Physics

## Degrees Granted

Y. Ito, Ph.D., Physics, June 1967
L. A. Schwarzkopf, B.S., Physics, June 1967

## Sponsorship

U. S. Atomic Energy Commission, AT(30-1)-3031, DSR 79210
National Science Foundation, Grant GP-6195, DSR 70038

## Research Report

### 1.0 Ferromagnetic Prism Refraction of Neutrons

Personnel: Professor C. G. Shull; C. S. Schneider

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

Studies have continued on refractive bending of neutrons in passing through ferromagnetic prisms which will serve as a means of determining the forward magnetic scattering amplitude in pure iron. Since these angular deflections are very small, at most of the order of 10 seconds arc, the high angular resolution in a double crystal spectrometer utilizing perfect silicon crystals is being exploited. Much effeort has been expended in calibrating the angular sensitivity and the positioning characteristics of the spectrometer through use of an optical interferometer system. This investigation has suggested some modifications in the spectrometer which are now being effected.

Studies of the Stern-Gerlach splitting of an unpolarized neutron beam into its two spin state components have been continued and a double Stern-Gerlach system has been studied. In the double-prism assembly, provision is available for rotating the polarization of the separated spin state beams through known angles thereby permitting a simple demonstration of the quantum-mechanical projection probabilities of a spin state when analyzed in a rotated system.

## 2.0 Refractive Bending of a Neutron Beam by a Magnetic Field

Personnel: Professor C. G. Shull; R. Ciszewski; C. Schneider

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

Studies similar to (A) have been performed with pure magnetic fields shaped with prism and cylindrical geometry. Deflection and focussing effects have been studied with field strengths up to 10 kilogauss and a neutron wavelength of 2.4 Angstroms and these have shown agreement with that expected by calculation. Lens action has been demonstrated and as expected this is found to be converging or diverging depending upon the neutron spin state.

## 3.0 High Temperature Study of Iron Magnetic Scattering

Personnel: R. Maglic

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

Measurements have started of the magnetic scattering amplitudes in several Bragg reflections from iron at temperatures through the Curie temperature. Polarized neutrons are being diffracted by pure iron crystals under minimal extinction conditions. An accurate comparison of the temperature dependence of magnetic scattering with the magnetization is being sought. Additionally, changes in the spatial asymmetry of the magnetic electrons with temperature are being searched for.

## 4.0 Coherent Paramagnetic Scattering by Vanadium in the Normal and Superconducting State

Personnel: Professor C. G. Shull; W. Just; C. Stassis

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

Previous work on the origin of the paramagnetic susceptibility of vanadium has shown it to arise from a polarization of the vanadium 3d electrons by the applied magnetic field. This induced magnetization is without temperature dependence down to the superconducting transition. Polarized neutron experiments have been started to assess whether there is any evidence of electron spin-pairing below the transition as has been found in similar experiments on superconducting $V_3Si$. Several specimen crystals have been studied all of which are of purity indicated by resistance ratio values of about 20. In the near future, crystals of higher resistance ratio (100 or 150) will be available and the studies will continue with these.

## 5.0 Electric Dipole Moment of the Neutron

Personnel: Professor C. G. Shull

Sponsorship: U. S. Atomic Energy Commission, AT(30-1)-3031, DSR 79210

Studies have continued in the search for the existence of an intrinsic electric dipole moment for the neutron by a polarized beam scattering technique. If such an EDM exists because of time-reversal-violation, there is to be expected an extra term in the amplitude of neutron scattering by an atom because of interaction between the EDM and the atom Coulombic fields. This can be sensed in very sensitive fashion by polarized neutron scattering from selected crystals. Work has concentrated on the (004) Bragg reflection from CdS crystals and the results, obtained at MIT and Brookhaven National Laboratory, have yielded an electric dipole length (figured with electron charges) of $+ 2.4 \pm 3.9 \cdot 10^{-22}$ cm. Thus no real effect has been measured but the upper limit which has been set is valuable in guiding the selection of conservation law theories.

## 6.0 Study of Non-Centrosymmetric Thermal Oscillation of Atoms in Germanium

Personnel: A. C. Nunes

Sponsorship: U. S. Atomic Energy Commission, AT(30-1)-3031, DSR 79210

Because of the tetrahedral atom configuration in the germanium crystal structure (diamond type) it has been suspected that the atoms partake of a non-spherical thermal oscillation. This is being sought experimentally by neutron diffraction intensity measurements of normally-forbidden Bragg reflections such as the (222). The experiments must be performed under conditions where parasitic effects, such as multiple Bragg reflection and higher order wavelength contributions, are absent. Progress to date has been with crystals at room temperature and a high temperature furnace is now being constructed which will permit enhancement of the thermal oscillation effects.

## 7.0 Neutron Diffraction Tests on Dynamical Theory

Personnel: Professor C. G. Shull

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

The spatial and angular characteristics of neutron beams Bragg reflected by perfect crystals of silicon are being investigated for comparison with dynamical theory predictions. Studies are being carried out with both transmitting and reflecting crystals as components in both single crystal and double crystal spectrometry. Because of the absence of true absorption in the neutron passage through these crystals, the dynamical theory of scattering, in which there is a continual transfer of beam energy between the forward direction and Bragg direction, can be tested in a unique way compared to the X-ray case.

## 8.0 Coherent Scattering Amplitude Studies

Personnel: W. Just; C. Schneider; L. Schwarzkopf

Sponsorship: National Science Foundation, Grant GP-6195, DSR 70038

As part of a continuing study of coherent scattering amplitudes by various atoms and isotopic nuclei, determinations have been carried out for zinc and its isotopes $Zn^{64}$, $Zn^{66}$, $Zn^{68}$ and for elemental copper. This has been performed by powder diffraction technique and, recently, attention has been given to the use of prism refraction measurements for this purpose.

## Theses

Y. Ito, "Spin Dependence of Thermal Neutron Nuclear Scattering by Cobalt," Ph.D., Department of Physics, June 1967.

L. Schwarzkopf, "Determination of Coherent Scattering Amplitudes of Separated Zinc Isotopes," B.S., Department of Physics, June 1967.

## Publications

C. G. Shull, K. W. Billman and F. A. Wedgwood, "Experimental Limit for the Neutron Charge," Phys. Rev. 153, 1415 (1967).

C. G. Shull, "Spin Density Distribution in Fe, Co and Ni," Symposium on Magnetic and Inelastic Scattering of Neutrons by Metals, Gordon and Breach Science Publishers, Inc., New York (1967).

C. G. Shull, "Neutron Interactions with Atoms," Trans. of Am. Crystal. Assoc. 3, 1-16 (1967).

C. G. Shull and R. Nathans, "Search for a Neutron Electric Dipole Moment by a Scattering Experiment," Phys. Rev. Lett. 19, 384 (1967).

## V. LOW TEMPERATURE PHYSICS

### Personnel

Dr. C. A. Shiffman, DSR Staff, Center fo Materials Science and Engineering
Dr. J. E. Neighbor, DSR Staff, Center for Materials Science and Engineering
Dr. R. C. Williamson, Visiting Scientist, Center for Materials Science and Engineering
Daryl A. Carnam, Research Assistant, Metallurgy
P. H. Haberland, Research Assistant, Physics
J. W. McWane, Research Assistant, Physics
R. F. Tinker, NSF Graduate Fellow, Physics
M. E. Malinowski, Senior Student, Physics
J. Michelson, Senior Student, Physics
J. Sandusky, Senior Student, Physics
H. Cronin, Technician, Center for Materials Science and Engineering
Gladys Lucian, Secretary, Center for Materials Science and Engineering

### Personnel who have left during the period

Dr. C. A. Shiffman, DSR Staff (Now at Northeastern University)
Dr. J. E. Neighbor, DSR Staff (Now at Northeastern University)
R. S. Newbower, DSR Staff (Now Graduate Student at Harvard University)
Daryl A. Carnam, Research Assistant (Now with Electronic Materials Laboratory, MIT)
P. H. Haberland, Research Assistant (Now at the Technical University, Berlin)
R. F. Tinker, NSF Graduate Fellow (Now at Research Laboratory of Electronics, MIT)
J. McWane, Research Assistant (Now at Research Laboratory of Electronics, MIT)
M. E. Malinowski, Senior Student (Now at the University of Illinois)
J. Michelson, Senior Student (Now at the University of Wisconsin)
J. Sandusky, Senior Student (Now at the University of Maryland)
H. Cronin, Technician (Now at NASA-ERC, Cambridge, Mass.)
Gladys Lucian, Secretary (Deceased)

Degrees Granted

M. E. Malinowski, S.B., Physics, June 1967

J. Michelson, S.B., Physics, June 1967

J. Sandusky, S.B., Physics, September 1967

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 788 )SR 75101

1.0 The Specific Heat of Superconductors

Personnel: Dr. C. A. Shiffman; Daryl A. Carnam

In collaboration with Professor H. C. Gatos we have been measuring the specific heats of a series of transition metal carbides. A complete report on these activities is contained in the Electronics Materials Laboratory report (H. C. Gatos), Section C-X.

2.0 Anomalous Skin Effect and Geometric Resonance (Radio Frequency Size Effect)

Personnel: Dr. C. A. Shiffman; P. H. Haberland

We have previously reported that the strength of certain RFSE resonances in gallium decreases as the temperature is reduced. Since it is generally assumed that the strength varies as $\exp(-1/\omega_c \tau)$, $\tau$ is the mean collision time and $\omega_c$ the cyclotron frequency), this anomalous behavior was very difficult to understand. We have recently been able to explain the "anomalous resonances", and to show in fact that they do not differ from "normal resonances" in any fundamental respect. The distinction between them is just the magnitude of the ratio of $\omega$ to $\omega_c$, where $\omega$ is the measuring frequency. Thus a resonance which is "normal" at one frequency becomes "anomalous" at another, and vice versa. We have demonstrated this by varying $\omega$ by almost a factor of 1,000, from 85kHz to 65MHz. We find that at fixed temperature the strength of a resonance has a flat plateau at low frequencies followed by a sharp decline as $\omega$ rises. If $\omega$ is low enough to lie in the plateau region the simple exponential behavior is observed in the temperature dependence; if $\omega$ is beyond the plateau various degrees of anomalous behavior are found.

The key to the understanding of these observations is the fact that in very pure metals an electron may make many cyclotron orbits before scattering, and hence may ultimately arrive in the skin layer out of phase with respect to the r.f. field. We have exploited this idea in a simple path-integral calculation of the strength of the resonance couched in terms of the quantities $x \equiv \pi/\omega_c \tau$ and $\theta \equiv 2\pi\omega/\omega_c$. The theory gives very good agreement with the observed dependencies on $\omega$ and $\tau$. From the frequency dependence it is possible to extract fairly accurate estimates (i.e. 30 to 50%) of $\omega_c$ and $\tau$ at a given temperature, and from the temperature dependence one can determine the relationship $\tau(T)$. Values of effective mass deduced from $\omega_c$ and the field at which the resonance occurs agree quite well with data from cyclotron resonance and deHaas van Alphen experiments. Values of $\tau$ are in keeping with estimates based on the d.c. conductivity, but show a strong (up to a factor of 10) variation from one extremal orbit to another on the Fermi surface.

## 3.0 Electrical Resistivity and Calorimetric Behavior of Pure Gallium near 1.7°K

Personnel: Drs. C. A. Shiffman, J. E. Neighbor

Newbower and Neighbor recently reported the discovery of an anomaly in the electrical resistance of large single crystals of very pure gallium. They found that the resistance in zero magnetic field has a narrow plateau near 1.7°K, which is displaced to lo r temperatures as the field is increased. We have carried out very precise alorimetric measurements which show that there is no corresponding anomaly in the specific heat of gallium. The heat capacity, C, was measured using the continouus-warming method and apparatus developed previously in this laboratory. Several high-resolution runs (temperature steps less than 0.005°K) over the temperature range 1.1-2.3°K failed to disclose any significant fine structure in the function C(T). In view of the depression of the resistive anomaly to lower temperatures with increasing magnetic field it was clearly advantageous to compare heat capacity data taken in zero field with data taken in various external fields. If the anomaly were indeed caused by a phase transition such a comparison would indicate directly the associated change of entropy, $\Delta S$. On the contrary our results establish the very small upper limit $\Delta S/\gamma T \leq 6 \times 10^{-5}$, where $\gamma T$ is the normal electronic entropy.

The above facts are of interest because they virtually rule out the possibility of a bulk phase transition in gallium near 1.7°K, including in particular, an antiferromagnetic transition. It should be noted in this context that even if we were dealing with spin-density wave antiferromagnetism we would expect the associated change in electronic entropy to be of the same order as the increment in resistivity, e.g. a few per cent. Such is not the case, so one may assume that the peculiar resistive behavior is a "pure" transport phenomenon.

## 4.0 Properties of Metals at High Pressures and Low Temperatures

Personnel: Dr. C. A. Shiffman; J. McWane

We have previously described a novel high pressure-low temperature apparatus which uses a bellows pressurized with liquid helium to drive a piston intensifier immersed in the helium bath. Solid helium is used as the pressure transmitting "fluid". In this apparatus the only connection between the high and low temperature parts of the system are the capillary tubes carrying relatively low pressures to the bellows and sample space. A number of experiments have been done to check the accuracy and reproduceability of the system as a whole, to test the reliability of the bellows assembly and to explore the nature and magnitude of the strains on specimens in the quasi-hydrostatic environment in the high pressure chamber. The bellows functioned perfectly in 80 cyclings to full pressure at 4.2°K or below over the course of the year. In every respect their performance was ideal, except for a small but reproduceable hysteresis, in the effective spring constant. These observations commend the bellows principle to applications where uni-axial stress is desired. In particular, for experiments on metals where large strains are not encountered, a bellows apparatus would be especially simple and advantageous. (Our system required four bellows in series because of the high compressibility of solidified gases.)

By far the most serious problem was the lack of true hydrostatic conditions in the bomb. (This failing is characteristic of all piston type systems using solidified gases as the pressure transmitting medium.) In order to explore this we have made measurements of the shift in transition temperature of indium with pressure, using solid-helium as the transmitting "fluid". Three techniques were used: (1) c.c. electrical resistance (2) mutual inductance at 23 cps of a coil system containing the specimen, and (3) surface impedance at 700kHz. In all three types of experiment the values of the shift in $T_c$ agreed with each other and with curves taken from the literature. The width of the transition appears to increase with increasing frequency, however. Since the frequency determines the depth of penetration of the measuring currents (in the normal state) these results indicate that there is a strong gradient in the strain at the surface of the specimen.

## Publications

W. D. Gregory, T. P. Sheahen and J. F. Cochran, "The Superconducting Transition and Critical Field of Pure Gallium Single Crystals", Phys. Rev. 150, 315 (1966).

J. McWane, J. E. Neighbor and R. S. Newbower, "Ultrasensitive Potentiometer for Use at Liquid Helium Temperatures", Rev. Sci. Instr. 37, 1602 (1967).

R. S. Newbower and J. E. Neighbor "Anomalous Resistance of Pure Gallium near 1.7°K", Phys. Rev. Letters, 18, 538 (1967).

J. E. Neighbor, J. F. Cochran and C. A. Shiffman, "Specific Heat of Lead in the Range from 2 to 8°K", Phys. Rev. 155, 384 (1967).

J. E. Neighbor and C. A. Shiffman, "Calorimeter Evidence for the Absence of Magnetic Phase Transition in Gallium near 1.7°K", Phys. Rev. Letters 19, 640 (1967).

P. H. Haberland and C. A. Shiffman, "Temperature and Frequency Dependence of the Amplitude of the Radio Frequency Size Effect in Gallium," Phys. Rev. Letters, 19, 1337 (1967).

# VI. ORDER-DISORDER PHENOMENA

## Personnel

Professor C. W. Garland, Associate Professor, Chemistry
D. Eden, Teaching Assistant, Chemistry
P. E. Mueller, American Can Company Fellow, Chemistry
R. T. Ruettinger, Research Assistant, Chemistry
N. E. Schumaker, Research Assistant, Chemistry
D. D. Snyder, Research Assistant, Chemistry
B. B. Weiner, Research Assistant, Chemistry
R. A. Young, Research Assistant, Chemistry

## Personnel who have left during the period

Dr. D. B. Novotny, Research Associate, Chemistry

## Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75104, 78880
National Science Foundation Grant, GP-5042, DSR 76047
Research Laboratory of Electronics, supported by the Joint Services Electronics Program under Contract DA28-043-AMC-02536(E), DSR 70050

## Research Report

### 1.0 Ultrasonics

During the past year, considerable progress has been made on all five projects mentioned in the last report. Indeed, the work on $NH_4Br$ and potassium dihydrogen phosphate (KDP) is now essentially complete.

During our high-pressure work on $NH_4Br$ at low temperatures, a new ordered phase was discovered in the region $T \sim 180$ to $230^{\circ}K$ and $p > 2000$ bar. The acoustic properties of this phase were completely determined, and the regions of the phase-transition lines were carefully studied. Data are now available on the previously known disordered cubic-ordered tetragonal lambda transition as well as the new order-disorder lambda transition and the order-order transition between the new high-pressure phase and the low-pressure tetragonal phase. X-ray and infrared data have also been obtained at 1 bar for temperatures down to 20$^{o}$K. In contrast to the much simpler system $NH_4Cl$, the $NH_4Br$ results clearly show that many complexities can occur in cooperative phenomena involving orientational ordering.

Ultrasonic measurements are now complete on KDP in the para-electric phase above its Curie point ($T_c$ = 121.8$^{o}$K). Data on the shear velocity as a function of temperature show that $c_{66}$ goes to zero at $T_c$ according to an elastic Curie-Weiss law. In addition, attenuation measurements were made at several frequencies and the ultrasonic loss was interpreted in terms of a very short, temperature-independent relaxation time ($\tau \sim 10^{-12}$sec). Data are not available below $T_c$, due to the very large acoustic losses between 90 and 122$^{o}$K. Such losses may be caused by domain scattering, in spite of the fact that a 3kV poling field was used. Further work on the ferroelectric phase using larger poling fields is in progress.

Velocity and attenuation measurements are currently being made on single-crystal quartz near its $\alpha$-$\beta$ transition at 847$^{o}$K. Since a pulse-echo method involving a long buffer rod is being used, only longitudinal waves can be measured with sufficient accuracy. Indeed, it has been necessary to develop a variety of new experimental techniques in order to carry out this work in the 500 - 600$^{o}$C region. Good uniformity and stability in the temperature of the sample has now been achieved, and a method of using molten AgCl acoustic seals has been developed. Longitudinal velocities in both the x and z directions show a sharp dip at the lambda temperature, but no clear indication of a discontinuity. Preliminary attenuation results indicate that the relaxation time for ordering in this system is quite long, perhaps on the order of $10^{-7}$ sec.

Interest in the liquid-vapor critical point is still very great, and work is in progress on xenon near its critical point at 16.6$^{o}$C and 58 bar. Recent measurements on helium suggest that the adiabatic sound velocity goes to zero at a critical point, in contradiction to the classical theoretical view that it will approach a finite minimum. We plan to measure the velocity for $\Delta T/T_c$ values as small as $3 \times 10^{-6}$ (an order of magnitude better than the helium work) in order to test this behavior. Accurate acoustic attenuation measurements are also planned over a wide range of frequencies in order to obtain information about the dynamical response of a fluid near its critical point. All the equipment for this work has been assembled and tested. Control and measurement of the temperature and pressure are excellent, and the ultrasonic gear is also working well. Unfortunately, there have been a series of difficulties with the variable-path cell. Troubles with filling and leaks in the cover plate have necessitated a redesign of several features of the cell. These modifications are almost finished, and measurements should begin soon.

In order to make direct measurements of the volume of a $NH_4Cl$ single crystal near its lambda point at high pressures, we have designed and built a special capacitance cell containing two 1pF capacitors. One capacitor is rigidly mounted and serves to determine the dielectric constant of the gas at each pressure. The other capacitor has a variable gap, since one of its parallel plates is attached to the $NH_4Cl$ crystal. When the sample length decreases the gap will increase by the same amount. Since the GR three-lead, precision bridge will detect capacitance changes of 1 part in $10^5$, this method provides a very sensitive means of studying volume changes. Later, the same gas-pressure cell can be used to measure ultrasonic attenuation as a function of pressure.

## 2.0 Infrared Spectroscopy

The IR spectra of normal and deuterated ammonium chloride and bromide have been investigated at 1 atm with special emphasis on features related to the librational motion of the ammonium ions and their cooperative ordering. $NH_4Cl$ ($ND_4Cl$) undergoes a cubic order-disorder lambda transition at $242^oK$ ($249^oK$). The ordering in $NH_4Br$ ($ND_4Br$) is more complex. At $235^oK$ ($214^oK$), there is a lambda transition between the disordered cubic and an ordered tetragonal structure. In the region 78 - $108^oK$ (158 - $167^oK$), there occurs a complicated, gradual order-order transition from the tetragonal structure to the ordered cubic phase. The spectra contain several features which are very sensitive to the structural and ordering changes occuring at this lower transition and permit us to clarify its detailed behavior.

The binary and tertiary overtones of the librational mode have been observed in the ordered phases of all four salts, and these frequency values can be interpreted in terms of an anharmonic potential for the torsional oscillation.

## Publications

C. W. Garland and R. Renard, "Ultrasonic Investigation of the Order-Disorder Transition in Ammonium Chloride," Critical Phenomena, Proceedings of a Conference held in Washington, D. C., April 1, 1965, NBS Misc. Publ. No. 273, pp. 202-210 (1966).

C. W. Garland and N. E. Shumaker, "Effect of Ordering on the Infrared Spectrum of Ammonium Chloride," J. of Phys. Chem. Solids, 28, 799 (1967).

C. W. Garland and R. A. Young, "Order-Disorder Phenomena VI: Anomalous Changes in the Volume of Ammonium Chloride", J. Chem. Phys. (in press).

## VII. MOLECULAR SPECTROSCOPY

### Personnel

Professor R. C. Lord, Professor, Chemistry
Dr. T. M. Hard, Research Associate, Chemistry
Dr. Y. Kyogoku, Research Associate, Chemistry
Dr. Mireille P. Yagupsky, Research Associate, Chemistry
Dr. R. F. Lake, Research Associate, Chemistry
Dr. Issei Harada, Research Associate, Chemistry
Dr. Soon Ng, Research Associate, Chemistry
J. Laane, National Science Foundation Predoctoral Fellow, Chemistry
G. O. Neely, Research Assistant, Chemistry
C. C. Milinois, Research Assistant, Chemistry
W. J. Adams, Research Assistant, Chemistry
L. A. Carreira, Research Assistant, Chemistry
C. W. Wickstrom, Teaching Assistant, Chemistry
Nai-Teng Yu, Research Fellow, Chemistry
T. L. Berman, Research Fellow, Chemistry
C. S. Blackwell, National Science Foundation Predoctoral Fellow, Chemistry
D. C. Luk, Teaching Assistant, Chemistry
Ruth C. Deininger, Secretary, Chemistry

### Degrees Granted

J. Laane, Ph.D., September, 1967
G. O. Neely, Ph.D., September, 1967
V. M. Bermudez, Jr., S.B., June, 1967
E. J. Shimshick, Jr., S.B., June, 1967

### Sponsorship

Spectroscopy Laboratory: National Science Foundation, GP-4923, DSR 76049

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## Research Report

## 1.0 Studies in Far Infrared Spectroscopy

### 1.1 Investigation of Molecules with Strongly Anharmonic Potential Functions

The study of far infrared spectra of ring compounds has produced a number of new and quite interesting results. Dr. Jaan Laane has set up two computer programs for the determination of potential-energy curves for the inversion process in four-membered rings. One of these is a simple program for calculation of vibrational eigenvalues and barrier heights from far infrared data. The other is a translation to the IBM 360 system of a more elaborate Japanese program prepared in the Department of Physical Chemistry at the University of Tokyo. This detailed program was written for the determination of geometrical parameters as well as eigenvalues and barrier heights and has proved extremely useful.

Dr. Laane has applied these programs to the interpretation of the rather complicated far infrared spectra of silacyclobutane and cyclopentene. The potential functions of these two molecules contain barriers to inversion of 1250 and 660 calories/mol respectively, and the dihedral angles determined from the potential are in good agreement with those measured by rotational spectroscopy.

Further investigations of four, five and higher membered ring systems are in progress.

### 1.2 Pure Rotational Far Infrared Spectra

The pure rotational spectra of the molecules $HN_3$, HNCO, HNCS and their deuterium derivatives have been studied in the range 20-250 $cm^{-1}$ with spectral slit widths of 0.2-0.5 $cm^{-1}$. Both the widely spaced $^RQ_K$ branches ($\Delta K = +1$) and the associated $^RR_K$ and $^RP_K$ branches were observed. For $HN_3$ the Q branches can be fitted reasonably well by first-order distortion theory, but higher-order treatment is required for HNCO and HNCS because of the unprecedentedly large centrifugal distortion. The reasons for this distortion and for the breakdown of the usual theoretical treatment have been examined by Dr. G. O. Neely. He has developed the theory for several simple models with extreme distortion and has been able to account for the magnitude of the observed distortion and for the apparently anomalous behavior of the distortion constant $D_{JK}$ found in microwave studies of these molecules.

## 2.0 Infrared and Raman Studies of Compounds of Biophysical Interest

The Raman spectra of aqueous solutions of a number of complementary base-pairs have been studied at neutral pH up to solute concentrations of 1 M. At these concentrations the Raman spectra of the mixtures are substantially the same as the superposition of the spectra of the components, that is, no specific base-pairing interaction is detectable. This is in contrast to the results of infrared studies of chloroform solution, where association can be seen at much lower concentrations (0.01 M). However, interaction between nucleosides and heavy-metal ions is readily observable; the system cytidine - $HgCl_2$, for example, has been studied and the equilibrium constant for the binding of $Hg^{++}$ to cytidine evaluated.

The addition of a laser to the Raman spectrometer has enabled the study of considerably smaller samples (~ 1 mg). Excellent spectra in the low-frequency region have been obtained of mixed crystals of DNA bases. Together with the far infrared spectra of these crystals the data yield valuable information about the strength of hydrogen bonding between the DNA bases. Laser-excited Raman spectra have also been studied in preliminary fashion for aqueous solutions of molecules of elevated molecular weight, specifically polyadenylic acid and lysozyme. Rather unsatisfactory spectra accompanied by a high background were obtained from these materials and further study is in progress to ascertain whether the difficulties are basic to the nature of the solute.

Studies of the association of DNA constituents and related molecules in chloroform solution by infrared spectroscopy were extended to a number of different compounds of biological interest. It was found, for example, that barbituric acid derivatives bind strongly to adenine, but not to the remaining DNA bases. Association constants of antibiotics and other drugs with the bases are being measured.

## 3.0 Instrumental Developments

The addition of the helium-cooled bolometer to the high-resolution far-infrared spectrometer has improved its performance, and further improvement seems possible with better preamplifiers. The spectrometer has its best performance in the region near 60 $cm^{-1}$, where the lines of the pure rotational water doublet at 59.871 and 59.939 $cm^{-1}$ were cleanly resolved with a signal-to-noise ratio of about 15:1 and a scanning speed of 0.03 $cm^{-1}$ per minute. The double-beam operation of the instrument has been a most valuable feature, and the instrument is in daily use on a variety of problems. Most of these have been with gaseous samples, but auxiliary equipment for the liquid and solid states is under development.

A commercial He-Ne laser of about 85 milliwatts CW power has been added to the recording Raman spectrometer (Cary Model 81). The laser source has completely supplanted the original mercury arc of this instrument because of its power, monochromaticity, polarization, small beam size and low photochemical activity. The laser possesses great advantage for biophysical spectroscopy by the small sample size required. It is hoped to add an argon-ion laser to the spectrometer to improve the excitation of spectra where the photochemical stability and color of the sample will permit the use of shorter exciting wavelengths.

## Theses

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G. O. Neely, "A High-Resolution Far-Infrared Study of Rotation in $HN_3$, HNCO and HNCS", Ph.D. Thesis, Department of Chemistry, August 1967.

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R. C. Lord and G. J. Thomas, Jr., "Raman Spectral Studies of Nucleic Acids. I. Ribonucleic Acid Derivatives", Spectrochimica Acta 23A, 2551 (1967).

R. C. Lord and G. J. Thomas, Jr., "Raman Spectral Studies of Nucleic Acids. II. Aqueous Purine and Pyrimidine Mixtures", Biochim. Biophys. Acta 142, 1 (1967).

J. Laane and R. C. Lord, "Far Infrared Spectra of Ring Compounds. II: Spectrum and Ring Puckering Potential of Cyclopentene", J. Chem. Phys. 47, 000 (1967).

J. Laane and R. C. Lord, "Far Infrared Spectra of Ring Compounds. III: Spectrum, Structure and Ring-Puckering Potential of Silacyclobutane", J. Chem. Phys. (in press).

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T. M. Hard and R. C. Lord, "A Double-Beam High-Resolution Spectrometer for the Far Infrared", Applied Optics (in press).

B. Krakow, R. C. Lord and G. O. Neely, "A High-Resolution Far-Infrared Study of Rotation in $HN_3$, HNCO, HNCS and Their Deuterium Derivatives", J. Mol. Spectry. (in press).

G. O. Neely, "Interpretation of Extreme Centrifugal Distortion in HNCO, HNCS and their Deuterium Derivatives", J. Mol. Spectry. (in press).

## VIII. INFRARED AND RAMAN SPECTROSCOPY OF SOLIDS

### Personnel

Professor C. H. Perry, Assistant Professor, Physics
Dr. R. P. Lowndes, DSR Staff, Research Laboratory of Electronics
Jeanne H. Fertel, Graduate Assistant, Physics
D. J. Muehlner, National Science Foundation Fellow, Physics
K. Owyang, Undergraduate Assistant, Physics
J. F. Parrish, National Science Foundation Fellow, Physics
N. E. Tornberg, Graduate Assistant, Physics

### Personnel who have left during period

J. G. Davis, Research Assistant, Electrical Engineering
S. Dreher III, Student Technician
L. R. Grubic, Jr., Undergraduate Assistant
E. M. Immerman, Undergraduate Assistant, Physics (Now in Physics Department, University of Maryland)
J. Z. Mase, Undergraduate Assistant, Physics (Now in Physics Department, University of California, Berkeley)

### Degrees Granted

J. F. Parrish, S.M., Physics, June 1967
E. M. Immerman, S.B., Physics, June 1967
J. Z. Mase, S.B., Physics, June 1967

### Sponsorship

Research Laboratory of Electronics. Supported in part by the Joint Services Electronics Program under Contract DA28-043 AMC-02536(E), DSR 70050
Air Force Cambridge Research Laboratories, AF19(628)-6066, DSR 70121
Spectroscopy Laboratory. Supported in part by the National Science Foundation, Grant Number GP-4923, DSR 76049. Optical Equipment Grant: MIT Sloan Fund for Basic Research.

## Research Report

The research activities of this group have been concentrated on the study of collective oscillations in solids determined by both infrared and Raman spectroscopy. The work can be summarized to some extent by the numerous publications and papers presented at various international meetings during the year.

### 1.0 Instrumentation

The measurements of the optical properties have been made using far infrared vacuum instruments, a Fourier transform spectrometer with low temperature detector and laser-Raman equipment. It is possible to obtain data from 2.5 - 1000 microns (4000-10 $cm^{-1}$) in the infrared over the temperature range 1.5 - 700°K using both transmission and variable angle reflection techniques. Computer programs are available for obtaining optical constant data using a Kramers-Kronig analysis and a classical dispersion model incorporating interaction damping can be used to fit the measured reflectance spectra. A He-Ne laser is presently used as the monochromatic source in the Raman studies and two argon lasers are under construction to provide additional flexibility and better signal to noise. It is hoped that a new double monochromator with photon counting will also be added in the near future. A variable temperature cryostat from 20 - 300°K with better than ± 0.3°K stability over this temperature range is now in operation in both the infrared and Raman apparatus. This additional facility will allow complete exploration in the region of phase changes.

### 2.0 Infrared and Raman Investigation

The materials investigated to obtain the phonon modes and optical properties include a complete analysis of CdS and CdSe mixed crystals. Investigations show a local mode and its second harmonic of S in CdSe and results indicate the presence of a gap mode of Se in CdS. Two fundamental lattice modes are observed over all concentrations and consistent two-phonon assignments of the bands observed from 230-600 $cm^{-1}$ has been made. In contrast only one mode behavior has been observed in KCl-KBr mixed crystals both in transmission and reflection although some evidence of additional structure has been observed at low temperatures. Observation of two magnon processes in some transition metal perovskite fluorides has so far been unsuccessful but further investigation is planned. However, many impurity induced resonances in the far infrared have been observed at $4^{\circ}K$ although the interpretation is difficult in view of the many bands and numerous impurities.

Some mixed ferroelectric crystals continue to be of interest and the second order Raman spectra have been interpreted in terms of a combined density of states curve resulting from critical points of the edge of a pseudo-Brillouin zone. "Soft" mode behavior can be seen from the infrared reflectance measurements but electric field induced Raman spectra would possibly lead to a more concise investigation. Other ferroelectric materials are presently being investigated together with a variety of mixed crystals including other alkali-halides and solidified inert gases. Some work is also in progress on both the electronic and phonon contributions to the infrared and Raman spectra of some materials containing rare-earths.

## Publications

C. H. Perry, D. P. Athans, E. F. Young, J. R. Durig, and B. R. Mitchell, "Far Infrared Spectra of Palladium Compounds. III Tetrahals, Tetraammine, and Dihalodiammine Complexes of Palladium (II)" Spectrochim. Acta. 23A, 1137 (1967).

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C. H. Perry and T. F. McNelly, "Ferroelectric 'Sofe' Mode in $KTaO_3$," Phys. Rev. 154, 456 (1967).

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C. H. Perry and E. F. Young, "Infrared Studies of Some Perovskite Fluorides (I) Fundamental Lattice Vibrations," J. Appl. Phys. 38, 4616 (1967).

E. F. Young and C. H. Perry, "Infrared Studies of Some Perovskite Fluorides II. Multiphonon Spectra," J. Appl. Phys. 38, 4624 (1967).

## Papers Presented at Meetings

C. H. Perry, "Dielectric Properties and Optical Phonons in $SrTiO_3$ and $KTaO_3$," Research Laboratory of Electronics, MIT, Annual

Research Review, May 3-5, 1967.

D. J. Muehlner and C. H. Perry, "Far Infrared Impurity Induced Absorption in $ABF_3$ Single Crystals," Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 5-9, 1967.

J. F. Parrish, C. H. Perry and S. S. Mitra, "Lattice Vibrational Spectra of CdS-CdSe Mixed Crystals," Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 5-9, 1967.

T. G. Davis, N. E. Tornberg, C. H. Perry and N. Knable, "Raman Spectra of Some Ferroelectric Crystals," Symposium on Molecular Structure and Spectroscopy, Ohio, September 5-9, 1967.

Jeanne H. Fertel, E. N. Immerman, and C. H. Perry, "Optical Phonons in Mixed Crystals of KCl-KBr," Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 5-9, 1967.

J. F. Parrish, C. H. Perry, S. S. Mitra and O. Brafman, "Phonons in $CdS_x Se_{1-x}$," American Physical Society Meeting on II-VI Semi-Conducting Compounds, Providence, Rhode Island, September 6-8, 1967, Proceedings p. 1164.

T. G. Davis, N. E. Tornberg, C. H. Perry and N. Knable, "Optical Phonons in Mixed Sodium-Potassium Tantalates," Symposium on the Molecular Dynamics and Structure of Solids, National Bureau of Standards, October 16-19, 1967.

## IX. RADIOFREQUENCY, MICROWAVE AND OPTICAL SPECTROSCOPY OF LIQUIDS: SOLIDS AND GASES

### Personnel

Professor G. B. Benedek, Professor, Physics
Professor J. D. Litster, Assistant Professor, Physics
Professor T. J. Greytak, Assistant Professor, Physics
J. B. Lastovka, DSR Staff, Center for Materials Science and Engineering
D. Cannell, Research Assistant, Physics
N. Clark, Research Assistant, Physics
S. B. Dubin, Research Assistant, Physics
J. Ho, Research Assistant, Physics
P. Lazay, Research Assistant, Physics
J. Lunacek, Research Assistant, Physics
R. St.Peters, Research Assistant, Physics
Malinda Rieck, Secretary, Center for Materials Science and Engineering

### Personnel who have left during the period

Dr. A. C. Saxman, DSR Staff (Now at Bell Telephone Laboratories, Whippany, New Jersey)
Gladys Lucian (Deceased)

### Degrees Granted

T. J. Greytak, Ph. D., Physics, February 1967
J. B. Lastovka, Ph. D., Physics, September 1967

### Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78880, DSR 75102
Sloan Fund for Basic Research in the Physical Sciences (Sloan Fund 27731) National Aeronautics and Space Administration, NGR-22-009-182, DSR 76375 U.S. Army Research Office-Durham, DH-31-124-ARO-D-425, DSR 76210

## 1.0 Brillouin Scattering in Liquids, Solids, and Gases

### 1.1 Brillouin Scattering Near the Critical Point of $NH_4Cl$

Personnel: Professor G. B. Benedek; P. Lazay

Object:

To study the temperature variation of the microwave frequency, elastic constants near the second order phase transition in $NH_4Cl$.

Research Report

We have measured the velocity of hypersonic longitudinal and transverse sound waves propagating in the <110> direction as a function of temperature from $-50^{\circ}C$ to $+50^{\circ}C$. In the neighborhood of the critical temperature ($T_{\lambda} = -30.4^{\circ}C$) the temperature intervals are as close as 2 millidegrees. The central component in the scattered light shows a very substantial depolarized component. We have found that both the polarized and depolarized components of the scattered light increases very markedly in the vicinity of the critical temperature. Detailed analyses of the spectrographic traces indicate that the Brillouin components have a measurable natural width. This observation is being investigated carefully in project 1.3.

### 1.2 Construction of a Single-Mode, Frequency-Stabilized, Helium Neon Laser

Personnel: Professor G. B. Benedek; N. Clark

Research Report

Using the modified "Michelson scheme" devised by Dr. Paul Smith of the Bell Telephone Laboratories, we have succeeded in putting into operation of long, single mode laser capable of delivering between 10 and 25 milliwatts of power. By piezo electric control of the mirrors and thermostatic control of the laser mount we have been able to secure operation of this single moded laser stabilized in frequency to $\sim \pm$ 10MHz over periods of several hours. This laser is now being used to study the lifetimes of thermally excited phonons in $NH_4Cl$ near room temperature.

## 1.3 Lifetimes of Hypersonic Sound Waves in Solid

Personnel: Professor G. B. Benedek; J. Lunacek

Object:

To determine the natural widths of the Brillouin components in the light scattered from solids.

### Research Report

Using the single mode laser described in Section (1.2), along with a low dark current photomultiplier, and a flat Fabry-Perot scanning spectrometer we are making measurements of the natural widths of the Brillouin components coming from longitudinal sound waves in $NH_4Cl$ at room temperature.

## 1.4 Brillouin Scattering in Gases

Personnel: Professors G. B. Benedek, T. Greytak

Object:

To obtain information on the time dependence of the molecular distribution functions for monatomic and polyatomic gases through a study of the spectrum of the scattered light.

### Research Report

We have studied the density fluctuation spectrum of monatomic and polyatomic gases over a range of wavelengths extending down to the order of the mean free path of the molecules. This allows us to study the transition from the long wavelength region where the fluctuations may be described by continuum hydrodynamics to the short wavelength region in which the kinetic theory of gases must be applied. The preliminary results (Phys. Rev. Letters 17, 179 (1966)) and those incorporated in the Ph.D. thesis of T. J. Greytak indicated systematic deviations from the theoretical results available at that time. More recent calculations (A. Sugawara and S. Yip, Physics of Fluids, September 1967) have been able to match the original experimental results to within the experimental uncertainty, and to predict additional features of the spectra that should be accessable to experimental verification. At present the experimental technique is being modified to achieve a higher spectral resolution and a great sensitivity.

## 1.5 Brillouin Scattering in Liquid Helium

Personnel: Professors G. B. Benedek, T. Greytak; R. St. Peters

Object:

To measure the velocity and lifetime of hypersonic sound waves in liquid helium below the lambda point.

### Research Report

We have observed the Brillouin scattering in liquid helium due to thermally excited phonons whose frequencies are near 700 mc. The velocity of these phonons has been measured with a precision of 1% from $1.6^{\circ}$K to the lambda point $T_{\lambda} = 2.16^{\circ}$K. Our velocities are in agreement with the acoustic results of Chase taken using 1 mc. driven sound. We are now working on extending our temperature range down to $1^{\circ}$K, on increasing our resolution in order to measure line widths, and on increasing our signal strength for greater accuracy.

## 1.6 Spectrum of Light Scattered from a Pure Fluid Near to Critical Point

Personnel: Professor G. B. Benedek; Dr. A. Saxman

Object:

To measure the line width ($\Gamma$) of the central component of the spectrum of light scattered from $SF_6$ near the critical point. And to deduce from this data the temperature and density dependence of the specific heat and the thermal conductivity.

### Research Report

We have measured the temperature dependence of $\Gamma$ along 7 isochores including the critical isochore. We have also measured the temperature dependence of $\Gamma$ along both the gas and liquid sides of the coexistence line. Finally we have obtained the density dependence of $\Gamma$ along the critical isotherm. From these data and our own precise measurements of the shape of the coexistence line, we have deduced the volume and temperature and the thermal conductivity ($\Lambda$) in the critical region. We find a strong divergence in the volume dependence at constant volume. This research is now being prepared for publication.

## 1.7 Brillouin Spectrum of a Fluid Near its Critical Po'nt

Personnel: Professor G. B. Benedek; D. Cannell

Object:

To determine the attenuation and velocity of thermally excited soundwaves in a fluid near its critical point.

Research Report

We have successfully carried out initial measurements of the collapse of the Brillouin components as the critical point is approached. In order to avoid the serious masking of the Brillouin components by the wings of the central component we have in construction a narrow bnnd optical filter for this unwanted component. Tests of this new device are now under way.

## 1.8 Heterodyne Detection of the Rayleigh and Brillouin Spectrum

Personnel: Professor G. B. Benedek; J. B. Lastovka

Object:

To use heterodyne beating techniques to study the line width of light scattered by entropy fluctuations and by thermally excited sound waves in liquids.

Research Report

Our measurements of the angular dependence of the central component line width of light scattered from toluene has been published (Phys. Rev. Lett. 17, 1039 (1966)). A detailed study of the signal to noise properties of optical mixing spectroscopy including both heterdyne and self beating spectrometers has been carried out in the thesis of Mr. J. B. Lastovka. This work will serve as the basis for future developments and applications of the techniques of optical mixing spectroscopy. Dr. Lastovka was granted the Ph. D. in Physics in September 1967.

1.9 Spectrum of Light Quasi-Elastically Scattered from High Molecular Weight Molecules

Personnel: Professor G. B. Benedek; J. Lunacek, S. Dubin

Research Report

Using a laser light sound in conjunction with an optical "self-beat" spectrometer whose resolving power is of the order of $10^{14}$, we have observed the spectral distribution of light scattered by dilute solutions of several natural and synthetic macromolecules, namely polystyrene latex spheres, bovine serum albumin, ovalbumin, lysozyme, tobacco mosaic virus, and deoxyribonucleic acid. From the spectrum of the scattered light, we have been able to determine the diffusion constants (D) of these macromolecules with a precision of typically 3 per cent.

This work has been published in Proc. Nat. Acad. Sci. 57, 1164 (1967).

2.0 Scattering of Light from Transparent Ferromagnets

2.1 Spectrum of Light Scattered from Thermally Excited Spin Waves in Ferrimagnets

Personnel: Professors G. B. Benedek, J. D. Litster

Object:

To detect the change in frequency of light scattered from a transparent ferrimagnet as a result of momentum and energy exchanges with spin waves.

Research Report

We have constructed and put into operation a high-resolution Fabry-Perot interferometer, a cooled housing for a near infrared photomultiplier tube, and have assembled a pulse height discrimination system. This system enables us to detect photocurrents as low as one electron per second. We have used it in conjunction with a $Nd^{3+}$: YAG laser at 1.06μ to detect the light scattered by thermal sound waves in water and KCl. The light scattered by magnetoelastic waves in YIG will be only slightly less intense, but we have been unable to detect it with our present samples because of the very intense scattering from imperfections. With improved samples we shall search for light scattered by acoustic magnons, phonons, and magnetoelastic waves in yttrium iron garnet.

## 2.2 Faraday Rotation in Magnetic Systems Near the Critical Point

Personnel: Professors G. B. Benedek, J. D. Litster; J. Ho, D. D. Berkner

Object:

To use the rotation of the plane of polarization to study the temperature dependence of the susceptibility of ferromagnets, and the field dependence of the magnetization, near the critical point.

Research Report

### 2.2.1. Faraday Rotation in $CrBr_3$

We have a dewar and temperature control system operating from 4.2°K to room temperature, and an optical system that enables us to measure the plane of polarization to about 0.003 degrees. Using this system and a pair of Helmholtz coils to provide small magnetic fields, we have observed the susceptibility diverge by a factor greater than 30 and follow the power law

$$\chi = D(T/Tc - 1)^{-\gamma}$$

with $\gamma$ - 1.21 over the temperature range

$$0.01 < \frac{T-Tc}{Tc} < 0.15$$

We have found it necessary to improve our temperature control to extend our measurements closer to Tc. In addition we are adapting an existing 12 inch Harvey Wells electromagnet to this experiment in order to be able to use a much wider range of magnetic fields. When these modifications are complete we shall continue to study the detailed behavior of $CrBr_3$ near Tc.

### 2.2.2. Faraday Rotation in YIG

We are also carrying out a similar experiment in YIG in the near infrared spectral region. An optical system similar to that used in $CrBr_3$ has been designed for use with a twelve inch electromagnet in the near infrared (1.15μ) region of the spectrum. This system is nearly ready for testing and will soon be in operation. With it we shall study the magnetic behavior of YIG in the critical region.

We plan to extend these measurements to other materials.

## Theses

J. F. Greytak, "Spectrum of Light Scattered from Thermal Fluctuations in Gases," Ph.D. Thesis, Department of Physics, February 1967.

J. B. Lastovka, "Light Mixing Spectroscopy and the Spectrum of Light Scattered by Thermal Fluctuations in Liquids," Ph.D. Thesis, Department of Physics, September 1967.

## Publications

K. Fritsch and G. B. Benedek, "Brillouin Scattering in Cubic Crystals," Phys. Rev. 149, 647, September 1966.

J. B. Lastovka and G. B. Benedek, "Spectrum of Light Scattered Quasi-elastically from a Normal Liquid," Phys. Rev. Lett. 20, 1039 (1966).

S. B. Dubin, J. H. Lunacek, and G. B. Benedek, "Observation of the Spectrum of Light Scattered by Solutions of Biological Macromolecules," Proc. Nat. Academy of Sciences, 57, 1164, May 1967.

G. B. Benedek, "Thermal Fluctuations and the Scattering of Light," Lecture Notes from Brandeis Summer Institute of Theoretical Physics (1966).

# X. SEMICONDUCTORS AND INFRARED SPECTROSCOPY

## Personnel

Professor R. A. Smith, Professor, Physics
Professor F. A. Johnson, Visiting Professor, Physics
Dr. S. Zwerdling, DSR Staff, Center for Materials Science and Engineering
J. P. Theriault, Engineering Assistant, Center for Materials Science and Engineering
F. Q. Yee, Engineering Assistant, Center for Materials Science and Engineering
Marion A. Curley, Secretary, Center for Materials Science and Engineering

## Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78880, DSR 75103

## Research Report

### 1.0 Spectroscopy in the Very-far Infrared

#### (a) Long-wave pass cryogenic filters for the very-far infrared

The transmittance spectra of two far-infrared long-wave pass filters of the powdered salt in polyethylene type first described by Yamada et. al. were measured at 296°, 77°, and 4.2°K. Such filters are required to prevent radiation of wavelength less than a particular value from entering an optical system, and must function without a light leak in the opacity region, with a sharp cut-on characteristic, and with high transmittance toward longer wavelengths in the pass-region. For the use with a cryogenic bolometer detector (see below) these properties were required at liquid helium temperature to eliminate undesired radiation from the room and other sources. These filters performed very satisfactorily, with a significant gratuitous improvement at low temperatures in their cut-on and transmittance characteristics relative to that at room temperature. The filters are made by laminating in a heated press thin polyethylene sheets each containing one of five or six different far-infrared reststrahlen-active salts, uniformly dispersed. The filter containing NaCl, KCl, KBr, KI and CsBr showed at 4.2°K a cut-on at 124μm, and a sharp rise in transmittance, the "knee" ending at ~165μm, and the transmittance reaching a maximum of 77% beyond 200μm. The second filter containing an additional CsI lamination, showed at 4.2°K a cut-on at 147μm, again a sharp rise, the "knee" now ending at ~190μm and the transmittance maximum reaching 65% beyond 200μm.

(b) Detectors for the very-far infrared

There is a great need for a fairly fast detector with nearly uniform response over the wavelength range 100 μ - 1000μ. The single-crystal bolometer would appear to offer attractive possibilities but as constructed so far these are rather slow in response. By using a very thin flake of material for the sensitive element the time constant may be reduced but, for the kind of crystal normally used, the absorption of the incident radiation would be either prohibitively small or the temperature coefficient of resistance small. Two methods have been used to overcome this defect - (i) by use of special material in the form of compensated Ge (see below) we obtain both a large absorption coefficient and high temperature coefficient of resistance (ii) by incorporating the sensitive element in a special optical system including a small integrating sphere and operating at pumped-helium temperatures an appreciable fraction of the incident radiation is absorbed.

A bolometer based on these principles has been constructed and carefully tested at 1.5°K. Absolute measurements of the 500°K blackbody responsivity, noise spectrum and detectivity for $\lambda > 150$ μm, their variations with frequency from 25-1000 Hz, the optimum bias current and the associated time constant, as well as the thermal parameters of the bolometer have been made. The bolometer behaves very much as was expected from its design. It has a far-infrared detectivity $D = 5 \times 10^{11}$ $Hz^{1/2}/W$ at 400 Hz, rising to $6.2 \times 10^{11}$ $Hz^{1/2}/W$ at 1 kHz, and a response time constant of 230μs. This bolometer when used with a suitable preamplifier allows operation beyond the "1/f" noise regions of both detector and preamplifier. A specially-designed ultra-low noise preamplifier has been constructed and tested along with the bolometer, yielding very satisfactory results.

## 2.0 Far-infrared Absorption in Semiconductors

Measurements of the absorption by single crystals of Ge simultaneously doped with various proportions of both n- and p-type impurities have been made in the far infrared. The absorption coefficient hardly varies between 4.2°K and 1.7°K in sharp contrast to the d.c. conductivity which decreases by an order of magnitude. Only a slight increase in absorption is found between 300μm and 825μm.

It is planned to extend these measurements and also to make similar measurements with doubly-doped Si.

## 3.0 The Quantum Theory of Lattice Dynamics

Personnel: Professor F. A. Johnson

The adiabatic approximation allows one to split the crystal hamiltonian into two nearly independent parts, namely the electronic and the phonon hamiltonians which have relatively weak coupling between them. The effective potential function in the phonon hamiltonian contains three contributions: (i) the direct nuclear-nuclear electrostatic interaction, (ii) the total adiabatic energy of the electrons and (iii) a small center of mass type correction which arises from the fact that the kinetic energy of the electrons and nuclii cannot be completely independent variables. When this effective potential energy function is expanded in powers of displacements from the equilibrium configuration, the zero order terms define the binding energy, the first order terms define crystal stability requirements, the second order terms define the phonon spectrum and the third order terms the phonon-phonon coupling.

The contributions of the direct nuclear-nuclear interaction to the various terms in the potential energy expansion can be readily evaluated but the contribution of the electronic system is more difficult. One makes the Hartree-Fock approximation and assumes that the many-electron wave functions can be expressed as antisymmetric determinants of single electron wave functions that are solutions of the coupled Hartree-Fock equations. This allows one to express the total electronic energy in terms of single-electron energies and wave functions and one can then proceed to expand this in powers of displacements. The electronic contribution to the first, second and third order terms can then be expressed in terms of virtual electron-phonon interactions. The first order terms arise from electron-one phonon matrix elements, the second order terms from a combination of repeated electron-one phonon and electron-two phonon matrix elements and the third order terms arise from electron-three phonon and combinations of electron-two phonon and electron-one phonon matrix elements.

The electron-two phonon matrix elements contribute a q-independent attractive potential to the dynamical matrix and the repeated electron-single phonon matrix elements contribute a q-dependent repulsive potential. As q tends to zero for acoustic modes these two contributions cancel, but as q increases the repulsive contribution changes and the resulting dispersion is largely determined by the electronic band structure.

The optical properties of phonons arise from the interaction of an external electric field with the electronic terms, and the infra-red and Raman lattice bands arise from exactly the same electron-phonon matrix elements as define the dynamical matrix itself.

Meeting Papers

S. Zwerdling, R. A. Smith, J. P. Theriault, and D. S. Mundel, "Theory and Development of a Fast High-Responsivity Single Crystal Germanium Far-Infrared Detector," Amer. Phys. Soc. Meeting Toronto, Canada (June 1967); Bull. A.P.S. Ser. III, Vol. 12, No. 5, p. 460 (May 1967).

S. Zwerdling, R. A. Smith, J. P. Theriault and D. S. Mundel, "Theory and Development of a Fast High-Responsivity Compensated Germanium Far-Infrared Detector," Symposium on Molecular Structure and Spectroscopy, Ohio State University, Paper Q8, Columbus, Ohio, September 8, 1967.

Publications

S. Zwerdling, J. P. Theriault and H. S. Reichard, "An Ultra-Low Noise Preamplifier for a High Impedance Cryogenic Bolometer", Infrared Physics (submitted for publication).

S. Zwerdling and J. P. Theriault, "The Low-Temperature Transmittance of Two Far-Infrared LWP Filters", Appl. Optics (submitted for publication).

R. A. Smith, F. E. Jones and R. P. Chasmar, Detection and Measurement of Infra-red Radiation, (2nd Edition). Announced by Oxford University Press in their Fall Catalogue.

# XI. MICROWAVE SPECTROSCOPY

## Personnel

Professor M. W. P. Strandberg, Professor, Physics
Professor R. L. Kyhl, Professor, Electrical Engineering
Dr. S. R. Reznek, DSR Staff
J. G. Ingersoll, DSR Staff
J. D. Kierstead, DSR Staff
J. B. Barton, Teaching Assistant, Physics
M. Ditz, Research Assistant, Chemical Engineering
R. L. Espino, Research Assistant, Chemical Engineering
L. Fox, Research Assistant, Physics
J. Free, Research Assistant, Physics
R. M. Langdon, Jr., Research Assistant, Physics
M. K. Maul, Research Assistant, Electrical Engineering
B. Yung, Research Assistant, Physics
M. J. Markovits, Undergraduate Thesis Student, Physics
R. Olsen, Master's Thesis Student, Electrical Engineering
T. A. Postol, Undergraduate Thesis Student, Physics
S. R. Kutner, Undergraduate Thesis Student, Physics
S. C. Schaffner, Undergraduate Thesis Student, Physics
C. Friedberg, Undergraduate Thesis Student, Physics
W. J. Schwabe, Senior Technician
Vera Conwicke, Secretary

## Degrees Granted

S. R. Reznek, Ph. D., Physics, September 1967
T. A. Postol, B. S., Physics, June 1967
S. Schaffner, B. S., Physics, June 1967

## Sponsorship

Research Laboratory of Electronics, supported in part by the Joint Services Electronics Program under Contract DA-28-043-AMC-02536(E), DSR 70050

## Research Report

The work of the Microwave Spectroscopy group is of several varieties.

### 1.0 Metals

Extremal sections of the Fermi surface of Ga, Cu, Sn are being measured using dimensional resonance. This technique observes the variation of electromagnetic surfact impedance of a metal single crystal at low temperatures when the electron orbit diameter, in a magnetic field, is equal to the crystal thickness in the plane of the orbit. Theoretical studies have been carried out to investigate the transport properties of these crystals under the conditions imposed by the experiment. Results on Ga indicate that APW band calculations are essentially correct.

### 2.0 Electron Paramagnetic Resonance

This work is mainly interdisciplinary. Research in cooperation with the Chemical Engineering Department has measured the reaction rate constant for atomic hydrogen reacting with solid propylene. The mechanics of the reaction have also been tentatively defined.

A study is being made of the mechanism of electric conduction in protein molecules.

### 3.0 Ultrasonics

A study of the boundary layer thermal resistance at metal-dielectric interfaces is being carried out. Also, acoustic propagation in metals at microwave frequencies is being studied to check out theoretical understanding of this process, and, in particular, the amount of acoustic absorption, i.e., the lattice-electron coupling in metals.

### 4.0 Superconducting Bolometers

These devices have been used as sensitive, fast detectors of acoustic and electromagnetic energy in our laboratory. The research on the device is directed to work on understanding of their noise properties.

Quarterly Progress Reports Research Laboratory of Electronics, MIT

M. W. P. Strandberg, "Electric Field Effects in the Nuclear Magnetic Resonance of Fluids," QPR No. 84, Pages 16-17, Research Laboratory of Electronics, MIT, January 15, 1967.

S. R. Reznek, "Expansion of Velocity Surfaces in Spherical Harmonics," QPR No. 84, Pages 17-26, Research Laboratory of Electronics, MIT, January 15, 1967.

R. L. Kyhl, "Ruby Cross Relaxation," QPR No. 84, Page 26, Research Laboratory of Electronics, MIT, January 15, 1967.

S. R. Reznek, "Velocity Surfaces in Lithium Niobate," QPR 85, Pages 5-12, Research Laboratory of Electronics, MIT, April 15, 1967.

M. W. P. Strandberg, "The Magnetic Field Dependence of the Temperature Coefficient of InSb's Hall Constant," QPR 86, Page 11, Research Laboratory of Electronics, MIT, July 15, 1967.

M. W. P. Strandberg, "Superconductive Tunneling, QPR No. 86, Pages 11-12, Research Laboratory of Electronics, MIT, July 15, 1967.

S. R. Reznek, "Green's Function Solution of the Boltzmann Equation in the Anomalous Skin-Depth Region," QPR 86, Pages 12-17, Research Laboratory of Electronics, MIT, July 15, 1967.

Theses

S. R. Reznek, "The Radio Frequency Size Effect in the Anomalous Skin Depth Region," Ph.D. Thesis, Department of Physics, September 1967.

T. A. Postol, "The Magnetic Field Dependence of the Temperature Coefficient of InSb's Hall Constant," S.B. Thesis, Department of Physics, June 1967.

S. C. Schaffner, "Superconductive Tunneling," B.S. Thesis, Department of Physics, May 1967.

Publications

J. M. Andrews, Jr., and M. W. P. Strandberg, "Bolometric Detection of Coherent 9-GHz Longitudinal Phonons in X-Cut Quartz," Journal of Applied Physics 38, No. 6 (May 1967).

A. Fukumoto and M. W. P. Strandberg, "Fermi Surface in Gallium Determined From the Radio-Frequency Size Effect," Phys. Rev. 155, No. 3 (March 1967).

R. L. Kyhl and B. D. Nageswara Rao, "Effect of $Al^{27}$ on Electron Cross Relaxation in Ruby," Phys. Rev. 158, No. 2 (June 1967).

## Papers Submitted for Publication

R. L. Kyhl, "Fast Sensitive Smith Chart Plotter on Microwave Reflectometer," Review of Scientific Instruments."

## Meeting Papers Presented in 1967

"Paramagnetic Defects in Crystals," presented at the University of Gent summer course, Belgium, August 28-September 9, 1967, by M. W. P. Strandberg.

"Introduction to Paramagnetic Resonance," presented at the Istituto Superiore di Sanita summer course, Italy, September 11-September 15, 1967, by M. W. P. Strandberg.

# XII. OPTICAL AND INFRARED MASERS

## Personnel

Professor A. Javan, Professor, Physics
Professor A. Szoke, Associate Professor, Physics
Dr. D. Ramachandra Rao, Visiting Scientist, Physics
Dr. P. Bonczyk, DSR Staff, Physics
Dr. V. Daneu, DSR Staff, Visiting, Physics
Dr M. Feld, DSR Staff, Physics
Dr. S. Iwasa, DSR Staff, Physics
R. W. Solomon, Administrative Assistant, Physics
T. Ducas, Research Assistant, Physics
B. Feldman, Research Assistant, Physics
L. Hocker, Research Assistant, Physics
M. Kelly, Research Assistant, Physics
M. Kovacs, Research Assistant, Physics
J. Levine, Research Assistant, Physics
F. Missell, Research Assistant, Physics
J. Murray, Research Assistant, Physics
J. Parks, Research Assistant, Physics
C. Rhodes, NSF Regular Graduate Fellowship, Physics
P. Schroeder, Research Assistant, Physics
D. Sokoloff, NSF Fellowship, Physics
W. Ryan, Engineering Assistant, Physics
Ellen Desmond, Secretary, Physics
Mary Phipps, Secretary, Physics

## Personnel who have left during the period

Professor R. Chiao, Assistant Professor, Physics (Now at University of California, Berkeley)

Dr. R. Cordover, Research Assistant, Electrical Engineering (Now at Technological Investors Management Corp., New York, N. Y.)

Dr. F. DeMartini, DSR Staff, Physics (Now at Institut d'Optique, Orsay, France)

Dr. H. Schlossberg, Research Assistant, Physics (Now at Avco-Everett Research Laboratories, Everett, Mass.)

Dr. C. Sacchi, DSR Staff, Visiting, Physics (Now at Instituto di Fisica del Politecnico, Milano, Italy)

Professor C. H. Townes, Institute Professor (Now at University of California, Berkeley)

## Degrees Granted

R. Cordover, Ph. D., Electrical Engineering, June 1967

M. Feld, Ph. D., Physics, September 1967

H. Schlossberg, Ph. D., Physics, January 1967

L. Aronberg, B. S., Physics, June 1967

W. Belfer, B. S., Physics, June 1967

D. Seeley, B. S., Physics, June 1967

## Sponsorship

National Aeronautics and Space Agency, NsG-330, DSR 76148

National Aeronautics and Space Agency, Electronics Research Center, NGR 22-009-240, DSR 70382

Air Force Cambridge Research Laboratories, F 19(628)-67C-0074, DSR 70140

Office of Naval Research, Nonr-3963(22), DSR 74979; N000 14-67-A-0204-0014, DSR 70620

## Research Report

Laser group's research activities extend over a broad range of electro magnetic spectrum--from the submillimeter wave and the far infrared to the short wavelength ultraviolet. Attempts are made to introduce a unified approach in exploring a varied set of problems. These have required developments of vastly differing technologies where fundamental research objectives have, by necessity, evolved together with developments of related problems in applied research. Various activities of the group may be subdivided into several broad categories each consisting of several experiments:

A continuing goal has been to eventually introduce microwave absolute frequency measuring techniques into the optical range of spectrum. An important step has been taken in this direction through laser harmonic frequency mixing up to 100$\mu$; this has been done through realization, for the first time, of a frequency "multiplier chain with a laser link".

As an example, we have been able to mix the third harmonics of a 337$\mu$ HCN laser with another laser frequency, the water laser, at 118$\mu$. In this mixing experiment, an intermediate frequency in the microwave region is used. The absolute frequency of the 337$\mu$ HCN laser was determined previously by direct mixing with high harmonics of a microwave signal; this in turn allowed absolute frequency measurements of 118$\mu$ transition. These techniques have been used in precision spectroscopic measurements of far infrared molecular laser transitions in DCN and HCN. Considerable techniques have been developed in superheterodyne detection of far infrared radiation with intermediate frequencies lying in the microwave region. An experiment on precise determination of speed of light is underway; it involves simultaneous determination of absolute wavelength and frequency of an infrared laser radiation.

Several techniques have been developed and applied to precise determination of isotope shifts, hyperfine structures and fine structure of atomic spectra. These techniques are based on new spectroscopic principles in which nonlinearities of atomic resonances are utilized for the first time, to achieve high resolution. In these experiments, Doppler-broadening effects are entirely eliminated and the high resolution limits are determined by natural broadening (or collision) effects. Considerable theoretical work has also been done in formulating various aspects of the radiative processes underlying these experiments.

In the violet range of spectrum, high resolution spectroscopy has been achieved by taking advantage of line narrowing effect in very high gain laser media. In these cases, spontaneous emission obtained from an amplifying medium with high gain is observed without introducing the usual Fabry-Perot type feedback: the traveling wave line narrowing effect enables high resolution measurements with unsurpassed accuracy.

A variety of molecular relaxation and energy transfer processes are studied in the infrared. Techniques have been developed and applied to observe and study in detail diffusion of molecular vibration excitation through as gas and its subsequent deexcitation small collisions. Also important molecular vibrational decay through V-V or V-T processes are determined in deaail.

Oscillatory interband magnetoreflection spectra of single crystal and paralytic graphite are studied in detail. These studies are made with the help of a unique high sensitivity-high resolution gas laser spectrometer developed and perfected recently; it utilizes a preselected gas laser oscillainng among a set of discrete frequencies covering a range of 4$\mu$ to 30$\mu$.

## Theses

R. Cordover, "High Resolution Study of the Structure of Atomic Transitions Using Lasers", Ph. D. Thesis, Department of Electrical Engineering, June 1967.

M. Feld, "Spectroscopic Studies of Atomic Oxygen Using Gas Laser Techniques", Ph. D. Thesis, Department of Physics, September 1967.

H. Schlossberg, "Theory and Application of an Ultra-High Resolution Spectroscopic Technique Using a Gas Laser", Ph. D. Thesis, Department of Physics, January 1967.

L. Aronberg, "Measurement of Absorption Parameters in Ammonia Gas Using the 10.6$\mu$ $CO_2$ Laser", B.S. Thesis, Department of Physics, May 1967.

W. Belfer, "The Interaction of Infrared and Ultraviolet Transitions in a Nitrogen Laser", B.S. Thesis, Department of Physics, May 1967.

D. Seeley, "Application of the Xenon Laser as a Sensitive Magnetometer", B.S. Thesis, Department of Physics, May 1967.

## Publications

R. H. Cordover, P. A. Bonczyk and A. Javan, "Precise Isotope Shift Measurements Using Line Narrowing Induced by Laser Radiation," Phys. Rev. Letters 18, 730 (1967).

L. O. Hocker, D. Ramachandra Rao, and A. Javan, "Absolute Frequency Measurement of the 190$\mu$ and 194$\mu$ Gas Laser Transition", Phys. Letters, 24A, 12 (1967).

L. O. Hocker and A. Javan, "Absolute Frequency Measurements of New CW HCN Submillimeter Laser Lines," Phys. Letters 25A, 7 (1967).

L. O. Hocker and A. Javan, "Laser Harmonic Frequency Mixing of Two Different Far IR Laser Lines Up to 118", Phys. Letters, February 12, 1968.

M. Feld and A. Javan, "Frequency Spectrum of Spontaneous and Stimulated Line Narrowing Effects Induced by Laser Radiation", Phys. Rev. Letters, March 1968.

M. Kovacs, D. Ramachandra Rao and A. Javan, "Study of Diffusion and Wall Deexcitation Probability of $00^01$ State in $CO_2$", Submitted for publication, J. of Chem. Phys.

D. Ramachandra Rao, L. O. Hocker and A. Javan, "Spectroscopic Studies of 4.3 Transient Laser Oscillation in $CO_2$, Submitted for publication,

J. of Molecular Spectroscopy.

J. Murray and A. Javan, "Collision Effects on the Width of Spontaneous Raman Scattering in Hydrogen Gas", Bull. Am. Phys. So. 12, March 1967.

S. Iwasa and E. Burstein, "Resonance Absorption by Coupled Modes of Collective Cyclotron Excitations and LO Phonons in Polar Semiconductors," Bull. Am. Phys. 12, March 1967.

R. H. Cordover, P. A. Bonczyk and A. Javan, "Effects of Collision on Saturation Behavior of 6328-A He-Ne Laser Transition", Bull. Am. Phys. Soc. 12, March 1967.

G. W. Flynn, L. O. Hocker, A. Javan, and D. Ramachandra Rao, "Characteristics of 4.35$\mu$ Laser Oscillations in $CO_2$", Bull. Am. Phys. Soc., 12, March 1967.

T. K. Gustafson, F. DeMartini and C. H. Townes, "The Evolution of Intense Short Pulses in Non-Linear Optical Media", Bull. Am. Phys. Soc. 12, 5 May 1967.

C. A. Sacchi and C. H. Townes, "Explanation of the Angular and Spectral Distribution of Anti-Stokes Light Generated by Self Trapping in Liquids", Bull. Am. Phys. Soc., 12, 5, May 1967.

H. P. H. Grieneisen and C. A. Sacchi, "Frequency Broadening of Trapped Light in Small Filaments", Full. Am. Phys. Soc., 12, 5, May 1967.

V. Daneu, "Acceleration of Electrons by Laser Radiation," Bull. Am. Phys. Soc., 12, 5, May 1967.

R. Y. Chiao, J. D. Dodson, D. M. Irwin and T. K. Gustafson, "Kerr Effect Saturation and the Size of Small-Scale Trapped Filaments", Bull. Am. Phys. Soc., 12, 5, May 1967.

M. S. Feld, B. J. Feldman, and A. Javan, "Frequency Shifts of the Fine-Structure Oscillations of the 8446A Atomic Oxygen Laser", Bull. Am. Phys. Soc., 12, 5, May 1967.

G. W. Flynn, M. S. Feld and B. J. Feldman, "New Infrared Laser Transitions and g-Values in Atomic Oxygen", Bull. Am. Phys. Soc. 12, 5, May 1967.

J. S. Levine, P. A. Bonczyk, and A. Javan, "Precision hfs Measurement by a Hyperfine Level Crossing in a Gas Laser", Bull. Am. Phys. Soc., 12, 7, November 1967.

J. H. Parks, D. Ramachandra Rao, and A. Javan, "High Gain Ultraviolet Transitions in $N_2$". Bull. Am. Phys. Soc. 12, 7, November 1967.

M. Kovacs, D. Ramachandra Rao and A. Javan, "Study of Diffusion and Wall Deexcitation Probability of $00^{0}1$ State in $CO_2$", Bull. Am. Phys.

Soc., 12, 7, November 1967.

M. S. Feld and A. Javan, "Frequency Profile of Line Narrowing Induced by Laser Radiation", Bull. Am. Phys. Soc., 12, 7, November 1967.

P. R. Schroeder, S. Iwasa, M. S. Dresselhaus and A. Javan, "Band Parameter Determination in Pyrolytic Graphite Through Analysis of Laser Magnetoreflection Data", Bull. Am. Phys. Soc. 13, 2, February 1968.

L. O. Hocker and A. Javan, "Absolute Frequency Measurements of New CW DCN Submillimeter Laser Lines", Bull. Am. Phys. Soc. 13, 2, February 1968.

F. P. Missell, S. Iwasa, M. S. Dresselhaus, and A. Javan, "Line Shape Analysis of the Optical de Haas-Shubnikov Effect", Bull. Am. Phys. Soc. 13, 2, February 1968.

C. Rhodes, M. Kelly and A. Javan, "Collisional Relaxation of the $10^{0}0$ and $02^{0}0$ Levels in $CO_2$", Submitted for publication, Bull. Am. Phys. Soc.

# XIII. LOW ENERGY PHOTON COUNTER

## Personnel

Professor D. Kleppner, Professor, Physics
Dr. T. Myint, DSR Staff, Physics
P. A. Montgomery, Graduate Student, Physics

## Sponsorship

Advanced Research Projects Agency, Contract SD-90, DSR 75107

## Research Report

We are studying the feasibility of a thin film superconducting counting device which may allow detection of individual photons at energies below one electron volt. It would also have the capability of counting individual hydrogen atoms by detecting the recombination energy when an atom combines with a molecular species on the surface of the detector.

Our immediate aim is to try the detecting device using an alpha particle source in order to confirm operations of the superconducting circuit and of the associated electronics. During this past fall we have constructed a cryogenic facility and have initiated resistance measurements on thin tin films in the transition region. Initial results are promising, though the quality of the film is difficult to control. However, the good films should be adequate for initial evaluation of the device.

# XIV. INTERATOMIC AND INTERMOLECULAR FORCES

## Personnel

Professor I. Amdur, Professor, Chemistry
Dr. M. C. Fowler, Research Associate, Chemistry
Dr. E. Hulpke, Research Associate, Chemistry
R. N. Nelson, Graduate Fellow, Chemistry
R. L. Hance, Graduate Fellow, Chemistry
M. J. Engler, Research Assistant, Chemistry
S. E. Johnson, Research Assistant, Chemistry
R. R. Luise, Research Assistant, Chemistry
W. A. Peters, Teaching Assistant, Chemistry
J. L. Kopolow, Senior Thesis Student, Chemistry

## Personnel who have left during the period

Dr. F. Danon
G. Starkschall

## Degrees Granted

M. C. Fowler, Ph.D., Chemistry, September 1967
G. Starkschall, S.B., Chemistry, June 1967

## Sponsorship

Office of Naval Research N000-14-67-A-0204-004, DSR 70323
National Science Foundation, NSF-GP5099, DSR 76051

## Research Report

### 1.0 Experimental Determination of Intermolecular Forces from Scattering of High Velocity Molecular Beams

Personnel: Professor I. Amdur; Drs. F. Danon, M. Fowler, E. Hulpke; R. Nelson, S. Johnson, R. Luise, R. Hance, M. Engler, W. Peters J. Kopolow

Sponsorship: Office of Naval Research and National Science Foundation, NSF-GP5099, DSR 76051

Dr. Jordan, formerly associated with this group, Dr. Fowler and the principal investigator are writing up results on scattering of He and Ar beams in $H_2$, $D_2$ and HD. Since both Dr. Jordan and Dr. Fowler worked independently on several of these systems in different apparatuses, it has been decided that a single comprehensive paper describing the results of both researches would be more informative than two separate papers. Mr. Nelson has completed studies of the efficiences of different charge exchange gases, $H_2$, $CF_4$, $SF_6$, $SiF_4$, Kr and Xe in producing beams of fast H atoms and fast $H_2$ molecules from accelerated beams containing mixtures of $H^+$, $H_2^+$ and $H_3^+$.

Dr. Fowler is looking for effects of inelastic collisions (vibration excitation) when beams of fast inert atoms (He, Ar ... etc.) are passed through room temperature mixtures of potentially reactive gases ($H_2$-$O_2$, $C_2H_4$-$H_2$ ... ). Measurements of sound absorption in such mixtures suggest that translational-vibrational energy transfer may be relatively efficient in mixtures of this type. Mr. Peters has started his Ph. D. research by working with Dr. Fowler on this project.

Mr. Johnson, Mr. Hance and Dr. Hulpke have made substantial progress in the design and construction of a new apparatus for scattering of positive alkali ions and negative halide ions in rare gases and in some cases in alkali metal vapors. Mr. Engler has completed measurements on the following systems: He-$CH_4$ (repeat check), Ar-$CH_4$, He-$GeH_4$ and Ar-$GeH_4$ and is now analyzing and correlating his results.

Mr. Luise's theoretical work on attempts to find a rational procedure for deducing potentials for unlike systems from those of like systems has progressed to the point where it seems appropriate to check his deductions to date against appropriate experimental results. Since these are not yet available in the literature, he will undertake these scattering experiments himself.

Mr. Kopolow is building an apparatus for directly measuring fractionation which occurs when gas mixtures, used in a collision scattering chamber, leave the chamber by molecular flow to become part of the background gas of a scattering chamber. His results will be applicable to the researches of Dr. Fowler and Mr. Peters.

## 2.0 Determination of Intermolecular Forces from Gaseous Equilibrium and Transport Properties

Personnel: Professor I. Amdur; Dr. F. Danon

Sponsorship: National Science Foundation, NSF-GP5099, DSR 76051

Dr. Danon completed two theoretical investigations: "Average Potentials and the Viscosity of Dilute Polar Gaess" and "Initial Pressure Dependence of the Viscosity of Polar Gases". The results of these investigations are being prepared for publication. Dr. Danon is currently a member of the Department of Chemistry faculty at the University of Chile at Santiago.

### Theses

M. C. Fowler, "High Energy Scattering of Helium by the Molecular Hydrogen Isotopes", Ph. D. Thesis, Department of Chemistry, September 1967.

G. Starkschall, "Calculations of the Thermal Beam Effect", B.S. Thesis, Department of Chemistry, June 1967.

### Publications

I. Amdur, "Fast Beam Scattering Experiments", to appear as Chapter 3.2 Volume 7 of the Methods of Experimental Physics series, L. L. Marton, series editor, B. Bederson and W. L. Fite, volume editors, published by Academic Press, Inc., New York.

J. E. Jordan and I. Amdur, "Scattering of High-Velocity Neutral Particles. XIV. He-He Interaction below 1.1 Å", J. Chem. Phys., 46, 165 (1967).

I. Amdur, "Applications of Molecular Beams to the Measurement of Collision Cross Sections and to the Determination of Intermolecular Forces", Entropie 18, 73-78, November-December 1967.

I. Amdur, H. Inouye, J. Los and A. J. H. Boerboom, "Determination of Incomplete Total Cross Sections of Particles with Argon Electron Configurations, with Argon in the High Energy Range", Entropie 18, November-December 1967.

J. E. Jordan and I. Amdur, "Almost 'Head-on' Collisions in the Scattering of Fast Argon Atoms by Hydrogen Isotopes", J. Chem. Phys. 46, 4145-4146, 15 May 1967.

SECTION B

# ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES OF MATERIALS AND DEVICE APPLICATIONS

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## I. MATERIALS THEORY GROUP

### Personnel

Professor G. W. Pratt, Jr., Professor, Electrical Engineering
Professor D. Adler, Assistant Professor, Electrical Engineering
Professor L. W. Gruenberg, Assistant Professor, Electrical Engineering
Professor L. G. Ferreira, Research Affiliate, Electrical Engineering
D. D. Buss, Teaching Assistant, Electrical Engineering
L. Johnson, Graduate Student, Electrical Engineering
E. K. Li, Research Assistant, Electrical Engineering
M. S. Maltz, Research Assistant, Electrical Engineering
P. G. McMullin, Research Assistant, Electrical Engineering
N. J. Parada, Research Assistant, Electrical Engineering
C. G. Whitney, Graduate Assistant, Physics
H. P. H. Yuen, Research Assistant, Electrical Engineering
Susan M. Johnson, Secretary, Electrical Engineering

### Personnel who have left during the period

L. G. Caron, Research Assistant, Electrical Engineering (Now at Université de Sherbrooke, Canada)
J. Cheng, Whitney Fellowship, Electrical Engineering (Now at Harvard University)
S. Rabii, Research Associate, Electrical Engineering (Now at Monsanto Laboratories, St. Louis, Missouri)

### Degrees Granted

L. G. Caron, Ph.D., Electrical Engineering, September 1967
J. Cheng, S.B., S.M., Electrical Engineering, February 1968
H. P. H. Yuen, S.B., S.M., E.E., Electrical Engineering, September 1967
G. M. Bunce, S.B., Electrical Engineering, September 1967

### Sponsorship

Office of Naval Research, Nonr-1841(72); NRO18-106, DSR 78721

Advanced Research Projects Agency, SD-90, DSR 78881, 78891
Army Research Office(Durham), DA-31-124-ARO(D)-92, DSR 79489

## Research Report

### 1.0 Electronic and Optical Properties of Materials (Army, ARPA)

An experimental program is being carried out to quantitatively study the frequency modulation of a GaAs diode laser by ultrasonic waves previously achieved in this laboratory. This is being done in cooperation with Bell Laboratories. Frequency modulation is being attempted at a modulation frequency of approximately 1 Kmc and a quantitative measurement of the index of modulation is being made. A study of interference effects between fm sidebands is being conducted.

A means of achieving separate, non-communicating inverted populations in the same semiconductor cavity is being investigated. This relies on the lifting of the multivalley degeneracy in the Pb salts by an extremal, uniaxial stress. This can result in a single cavity emitting two or more independent spontaneous lines or above threshold acting as two or more independent lasers. Among device applications are a tunable infrared source, a stable local oscillator and an ultra-high speed optical flip-flop.

A $k \cdot p$ interpolation scheme capable of accurately reproducing the band structure of the Pb salts throughout the Brillouin zone has been developed. Using these results, a calculation is being made of $\epsilon(k, \omega)$ and being evaluated. The electron-phonon interaction which must be included is closely related to $\epsilon(k, \omega)$. By studying how the phonon spectrum depends on external pressure the high pressure phase change observed in the Pb salts can be explained.

### 2.0 Correlation in Narrow Bands - Equations of State - Ferromagnetism - Magneto-optical Study of As and Bi (ONR)

A new method of studying the Hubbard Hamiltonian has been devised which is a self-consistent cluster approach related to the Bethe-Peierls-Weiss scheme. It successfully exhibits a metal-insulator or Mott transition for the half-filled narrow band.

The properties of a dynamical system allowing motion of atoms on a space lattice and bonding between nearest neighbors have been studied yielding an equation of state resembling the Van der Waal's equation. Its properties are being investigated.

A study of the Fermi surface of Ni as determined by a self-consistent APW band calculation published by J. Connolly is being made to determine if a Hume-Rathery type mechanism stabilizes the ferromagnetic surface for the ferromagnetic state can be used tc estimate the Curie temperature for Ni.

The eigenstates and energies for a ring of H atoms is being investigated. Mattheiss studied a ring of 6 sites and 6 electrons. Our study asks what happens to the states and energies when one electron is removed. The object is to check the suggestion of Nagaoka that substantial changes can occur in the energies of high spin states on the removal of one electron from the half-filled band case.

The results of the magnetoreflection experiment in bismuth have been analyzed to yield the form of the magnetic energy levels. This represents both a simplification of the energy level scheme proposed by Baraff and an extension to $k_H$ dependent energy levels. Magnetoreflection experiments in arsenic have yielded 2 series of interband transitions, identified with 2 different points in the Brillouin zone. Some features of these experiments can be understood in terms of the Lin-Falicov pseudopotential calculation, but important changes in the band model are required to explain the experimental results.

## 3.0 Effects of Non-stoichiometry and Impurities on Electronically Motivated Phase Transitions

The recent model presented to account for electronically motivated semiconductor-to-metal transitions has been extended to include effects of donor and acceptor levels brought about by non-stoichiometry or impurities. The temperature of the first-order phase transition is found to decrease monotonically as the concentration of donors or acceptors increases. Above a critical concentration, the ground state energy of the metallic phase is lower than that of the semiconducting phase, and the crystal is metallic at all temperatures. For smaller impurity concentrations, finite bandwidth leads to the free carriers becoming degenerate at very low temperatures, allowing for the possibility of metallic behavior considerably below the transition temperature.

The model has been applied to the mixed $Ti_{2x}V_{2(1-x)}O_3$ system. The three major results of the theory are quantitatively verified. Theory and experiment can be combined to estimate a value of $m^* \sim 70$ for the effective mass of holes in semiconducting $V_2O_3$.

## Narrow Energy Band Theory

In order to find out whether the Mott localized state or the Slater itinerant state is a better description of the d-electrons of transition metal compounds, a tight binding calculation has been made of the ground state energies of a model for which both states are possible approximations to the true ground state. Both states result in an antiferromagnetic, insulating crystal at $T = 0$. The result is that the Mott state has lower energy only if the average intra-ionic Coulomb repulsion U is larger than the sum of half the antiferromagnetic exchange energy, I, and a term, proportional to the bandwidth, $\Delta$, which represents the Coulomb interactions between the d-electron and the ion cores and the total Coulomb interaction of the ion cores among themselves. This result can be written

$$U < \frac{I}{2} - K\Delta$$

As the crystal is pulled apart, $\Delta$ vanishes. Since U is usually much greater than I, the Mott state has lower energy in this limit. However, even for small bandwidths, in polar crystals the term representing the attraction between the oppositely charged ions is large and negative, and the Slater state can have lower ground state energy.

It has also been shown that a suggestion by Mott that the Slater model cannot exhibit a small number of free carriers is incorrect if the bandwidth is comparable to or larger than I.

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# II. SEMICONDUCTOR MATERIALS AND DEVICES

## Personnel

Professor R. B. Adler, Professor, Electrical Engineering
Professor R. H. Rediker, Professor, Electrical Engineering
Professor P. E. Gray, Associate Professor, Electrical Engineering
Professor D. H. Navon, Associate Professor (Visiting) Electrical Engineering
Professor A. C. Smith, Associate Professor, Electrical Engineering
Professor R. D. Thornton, Associate Professor, Electrical Engineering
Professor B. D. Wedlock, Associate Professor, Electrical Engineering
Professor F. O. Arntz, Assistant Professor, Electrical Engineering
Professor J. N. Churchill, Assistant Professor, Electrical Engineering
Professor J. S. Moore, Assistant Professor, Electrical Engineering
Professor S. D. Senturia, Assistant Professor, Electrical Engineering
Professor D. L. Smythe, Assistant Professor, Electrical Engineering
Professor J. N. Walpole, Assistant Professor, Electrical Engineering
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R. L. Guldi, NSF Fellow, Electrical Engineering
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H. St. Onge, Teaching Assistant, Electrical Engineering
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Berylee Schutz, Secretary (part time), Electrical Engineering
Jarmila Z. Hrbek, Secretary (part time), Electrical Engineering
Jean Gorrasi, Secretary (part time), Electrical Engineering

Personnel who have left during the period

J. S. Brownson, DSR Staff (Now at Lincoln Laboratory, MIT)
J. G. Calderone, Research Assistant (Now at Bell Telephone Laboratories)
A. W. Carlson, NASA Fellow (Now at Varian Associates)
E. D. Crosby, Research Assistant (Now at General Electric Company)
C. K. Erdelyi, Research Assistant (Now in industry)
D. C. Green, Research Assistant (Now at Sanders Associates)
S. H. L. Liu, Research Assistant (Now in doctoral study, Harvard University)
E. A. Miller, Research Assistant (Now at Fairchild Semiconductor, Inc.)
P. E. Norris, Research Assistant (Now in doctoral study, University of Colorado)
J. A. Rome, Research Assistant (Now in doctoral study, MIT)
T. E. Sharon, Research Assistant (Now at Graduate School, California Institute of Technology)
P. S. Showman, Research Assistant (Now at Hewlett-Packard Inc.)

Y. Yacoby, Assistant Professor (Now on the faculty, Hebrew University, Israel)

Degrees Granted

G. S. Almasi, Ph.D., Electrical Engineering, February 1967
A. W. Carlson, Ph.D., Electrical Engineering, June 1967
J. Shah, Ph.D., Physics, February 1967
D. L. Smythe, Ph.D., Electrical Engineering, February 1967
M. S. Adler, S.M., and E.E., Electrical Engineering, June 1967
J. G. Calderone, S.M., Electrical Engineering, September 1967
C. K. Erdelyi, S.M., Electrical Engineering, September 1967
C. R. Hewer, S.M., Electrical Engineering, February 1967
J. G. Kassakian, S.M. and E.E., Electrical Engineering, September 1967
S. H. L. Liu, S.M., Electrical Engineering, June 1967
E. A. Miller, S.M., Electrical Engineering, June 1967
P. E. Norris, S.M. and E.E., Electrical Engineering, June 1967
J. A. Rome, S.M. and E.E., Electrical Engineering, September 1967
P. S. Showman, S.M., Electrical Engineering, September 1967
S.M. Spitzer, S.M. and E.E., Electrical Engineering, June 1967
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E. D. Crosby, S.B., Electrical Engineering, June 1967
D. C. Green, S.B., Electrical Engineering, June 1967
T. E. Sharon, S.B., Electrical Engineering, February 1967

Sponsorship

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National Aeronautics and Space Administration·Electronics Research Center, NgR 22-009-234, DSR 70574
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NSF Research Initiation Grant, DSR 70393
GM Fellowship
MIT Sloan Fund for Basic Research

## Research Report

### Survey

The general theme of the work undertaken here is the relationship between electronic device capabilities and limitations, and the materials employed. These capabilities and limitations may be inherent in the material itself, or may stem from problems of technology associated with the material. Our efforts may therefore span the range from attempting the description of ultimate circuit performance of an existing or newly conceived device, in terms that relate closely to its structure, all the way to attacking technological problems of importance in determining ultimate device performance.

### 1.0 Effects of Electric Field on Optical Absorption

### 1.1 Franz-Keldysh Effect and Dynamical Trapping in Semi-Insulating GaAs

Personnel: Professors R. B. Adler, Y. Yacoby; J. Shah

Sponsorship: Advanced Research Projects Agency

This project has been completed, and the abstract of Mr. Shah's doctoral thesis is reported herewith:

The Franz-Keldysh effect (for applied square wave electric fields $\sim 5 \times 10^3$ V/cm.) at $77^oK$ in semi-insulating GaAs, in the vicinity of the fundamental optical absorption edge, was observed to be a slow function of time, contrary to theoretical expectations. This suggested that the actual field in the sample was non-uniform and time-dependent. This could be caused by AC polarization induced in the sample by the applied electric field because of the presence of traps and recombination centers in the sample.

In order to obtain a better understanding of the nature and characteristics of this AC polarization of the material, detailed AC photoconductivity experiments, like measuring photoconductivity spectrum, studying the kinetics of rise and decay curves, etc., an investigation of how the excitation of the sample by a high AC electric field or by light of photon energy less than the bandgap of GaAs affects the "intrinsic" photoconductivity has also been carried out. It was observed that the intrinsic photoconductivity is "enhanced" by such excitations and that at 77°K this enhancement persists for a long time after the excitation has been removed. The concept of "Optical Charge Transfer" has been invoked to explain the optical enhancement. A recent theory of Dussel and Bube predicting a reduction in the Coulomb-attractive capture cross-sections has been used to explain the electric-field-induced enhancement. It is shown that all other electric field effects, including the "geometrical effect" caused by the presence of "blocking" contacts, contribute negligibly to the electric-field-induced enhancement. All these results have been theoretically analyzed and a complex energy level scheme for the bandgap of semi-insulating GaAs has been developed. Characteristics of these levels and values of various parameters have been determined.

The problem of finding the exact electric field distribution has been formulated using theunderstanding of the material achieved through the pnotoconductivity studies. This problem has been solved analytically, under certain well-justified approximations for times much smaller than the time constants of the slow recombination centers in the material. This solution has then been extended qualitatively for very large times when a steady-state is reached. It is concluded that the field distribution becomes more uniform at long times because of the action of slow recombination centers. Finally, the results of the Franz-Keldysh measurements have been explained by using this theoretical analysis.

## 1.2 Electro-Reflectance in GaAs

Personnel: Professor F. O. Arntz; T. E. Sharon, D. Reinhard

Sponsorship: Advanced Research Projects Agency

The electro-reflectance of p-type GaAs has been studied using perturbing potentials applied with a transparent liquid electrolyte. Electro-reflectance in the spectral range of 2.75 eV to 3.15 eV was studied as a function of the magnitude of the AC voltage with or without a super-imposed DC bias. The results are quite similar to those reported by Seraphin* but differ with regard to the magnitudes of potentials necessary to obtain the effects. The blocking-contact method of Seraphin demanded much larger voltages to obtain equivalent fields in the samples.

A study of electro-absorption in impure GaAs with internal electric fields parallel to the incident surface is underway. Evidence relating to Redfield's model for the broadening of the absorption edge** by fields associated with impurities will be pursued.

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*B. O. Seraphim, Journal of Applied Physics, 37, 721 (1966).

**D. Redfield and M. A. Afromowitz, Applied Physics Letters 11, 138 (1967).

## 1.3 Two-Photon Franz-Keldysh Effect and Related Non-linear Optical Phenomena

Personnel: Professors J. N. Churchill, F. O. Arntz, R. B. Adler

Sponsorship: NSF Research Initiation Grant, Ford Foundation Fellowship, National Aeronautics and Space Administration

A substantial review and general simplification of the theory of the two-photon Franz-Keldysh effect worked out by Y. Yacoby has been carried out. In its present form the theory lends itself to comparison of this effect with other non-linear optical effects, and permits a clearer evaluation of the experimental possibilities.

In order to observe the two-photon Franz-Keldysh effect experimentally, one needs a laser whose wavelength and power capabilities satisfy a relationship first specified by Yacoby. It appears that currently available lasers in the desired frequency range do not have sufficient power to satisfy the specifications. The possibility of a modified experiment is presently being considered in which the two-photon effect would be aided by a static electric field. The static field should allow the laser requirements to be relaxed.

## 1.4 Electro-Absorption and Electro-Reflectance in $SrTiO_3$

Personnel: Professor F. O. Arntz; T. Kaplan

Sponsorship: National Aeronautics and Space Administration

Electro-absorption measurements on 100$\mu$ platelets of $SrTiO_3$ with uniform fields across the thickness exhibit a broad unresolved edge in differential absorption. Electro-reflectance measurements beyond the absorption edge with fields parallel to the surface do not yield structure as sharply resolved as reported for the more covalent materials. Low temperatures, etching of the incident surface, and variations in the measuring technique fail to improve the resolution appreciably. Presently these limitations are regarded as fundamental in nature.

## 1.5 Optically Pumped Absorption in II-VI Compounds

Personnel: Professor F. O. Arntz; L. Goodman

Sponsorship: Advanced Research Projects Agency

Sensitive experimental apparatus for the study in II-VI compounds of the change of optical absorption produced by pumping and bleaching radiations is nearing completion. A Beckman DK-1A spectrometer has been modified to serve this function, together with phase-lock amplifiers and signal-averaging equipment.

## 1.6 Electro-Reflectance in CdS

Personnel: Professors R. B. Adler, Y. Yacoby; H. St. Onge

Sponsorship: National Aeronautics and Space Administration

This work has been completed, and the abstract of Mr. St. Onge's Master's thesis is given herewith:

Fluorescence, reflection and electro-reflectance have been observed and studied in single crystals of cadmium sulfide. Known intrinisc exciton transitions have been identified and studied in reflection under the influence of an electric field. The electro-absorption data was determined from Kramers Kronig inversion of the electro-reflectance data. It is found that the exciton absorption lines broaden considerably under the influence of the electric field and shift towards the higher wavelengths. A comparison of the results is made with a recent theory of the effect. Details of sample preparation and experimental technique are presented.

## 2.0 Interaction of Successive Diffusions of P and B in Silicon ("Collector Dip")

Personnel: Professor R. B. Adler; J. Brownson, H. M. Pearce, E. Prahl

Sponsorship: Advanced Research Projects Agency

Attempts were made to reproduce in our laboratory the "retardation" effects observed by J. E. Lawrence in p-n-p double-diffused structures. We were not able to obtain the effect, although the total impurity content of the base seemed to be close to the values for which "retardation" should have occurred.

Through the kind offices of Dr. H. Sello, some of the actual samples prepared by Lawrence, with the "retardation" effect present, were sent to us for examination on the electron microprobe. These samples were described as havi.., been prepared by a somewhat different phosphorous base diffusion process than ours, and with a boron emitter diffusion at a much higher temperature.

Our electron microprobe scans of an angle-lapped section of the "retarded" samples showed no observable "precipitates" of phosphorous near either the emitter collector junctions, anywhere on the sample. However, the resolution of the beam (approximately 1 $\mu$), and threshold of detectability for phosphorous (approximately 1%) would have required a very strong effect if it were to have been observable at all. We are currently trying to reconcile the differences in observed results with the different diffusion processes, and thereby to account for both the "retardation" and "push" effects in a theory which also fits other available experimental data as well.

## 3.0 Effects of Strain from Passiv. ting Layers on Silicon

Personnel: Professor R. B. Adler; J. H. Serebrinsky; W. Gajda

Sponsorship: Advanced Research Projects Agency

A preliminary evaluation has been made by Mr. Serebrinsky of the interaction between a semiconductor and its passivating insulator via the stress fields usually present at the interface. A facility for depositing silicon nitride films by pyrolitic decomposition of silane was set up (in cooperation with Mr. J. M. Harris of Electronics Materials Group), and films were subsequently deposited on silicon; some additional time was devoted to the control of the film and calibration of the equipment. The character (elastic or plastic) of the deformation produced by the mismatch of expansion coefficients is currently under study.

A Lang camera is now fully operational, good results haveing been obtained by Mr. Gajda in the resolution of defects in silicon. Dislocations and the strain fields resulting from the thermal growth of $SiO_2$ and the growth of SiN films on Si substrates have been investigated using this technique. Considerable experimental work is being done in the quantitative measurement of diffracted intensity enhancement from imperfect crystalline regions.

Ion-implanted samples of silicon have been examined, with the result that there was no observable damage throughout the implanted region (although dislocation networks were observed at the edges of the implanted areas in some cases).

Experiments have also been carried out on integrated circuits, in an attempt to obtain some correlation between device performance and observable defects. No significant results have been obtained to date.

The camera has also proved useful in measuring strain as a function of position in a given sample. This is accomplished by measuring angular changes in the $K\alpha$ diffraction peak maximum as the sample is translated across the incident beam. This technique has been used to obtain a quantitative picture of the effects of $SiO_2$ and SiN growth on the substrates.

Work is being done by Mr. Gajda on formulating a dynamical theory of X-ray diffraction by imperfect crystals in order to enable one to fully understand the details which appear in X-ray topographs. Such a theory would allow a greater utilization of X-ray topography in the reliability assessment of semiconductor devices.

## 4.0 Thermophotovoltaic Energy Conversion

Personnel: Professors P. E. Gray, B. D. Wedlock; C. R. Hewes, J. G. Kassakian

Sponsorship: U. S. Army Electronics Command

This research is concerend with the use of germanium p-i-n diode structures as photovoltaic cells for use in thermophotovoltaic energy conversion applications. The work has been concerend primarily with the evaluation of the performance limits set by device parameters and fabrication techniques in two different p-i-n cell structures. In one structure the junctions are on the opposite planar faces of an intrinsic region; in the other structure both the p-type and n-type regions are on the same planar face of the intrinsic region.

Devices embodying each of these structural arrangements have been fabricated using both diffusion and alloy techniques for junction formation. The factors which limit collection efficiency, output voltage, and power output have been studied. Theoretical guidelines for device design have been formulated.

This work is continuing, with emphasis on fabrication and evaluation of the structure in which both junctions are interleaved on the same face of the intrinsic region.

## 5.0 High Injection Effects in Semiconductors

Personnel: Professors P. E. Gray, D. L. Smythe; D. C. Green, J. R. Lowney, T. Schlax, L. Castro

Sponsorship: U. S. Army Electronics Command

This research is concerned with charge-carrier transport and recombination parameters, and with the two-dimensional distribution and flow of charge carriers in semiconductors under high-injection conditions.

An investigation of the effect of carrier-carrier scattering on the mobility of carriers in germanium has been completed. This work was based on the observation, by infrared and potential-probe techniques, of the distribution of excess carriers in the intrinsic region of a p-i-n diode which is pulsed into forward bias; injection levels of $4 \times 10^{17}$ $cm^{-3}$ have been obtained at current densities of about $10^3$ amperes per $cm^2$. These measurements show that the sum of the hole and electron mobilities drops to half its low-level value at an injection level of $10^{17}$ $cm^{-3}$.

These experimental techniques are now being extended so that the p-i-n diode structure can be used for the dynamic measurement of the incremental recombination lifetime at correspondingly high injection levels.

The two-dimensional distributions of current density, electric field, and carrier concentrations within the active base region of a planar transistor are also under study. This investigation, which includes the entire range of injection levels of interest in device behavior, does <u>not</u> make the usual assumptions which permit the resolution of the high-level two-dimensional problem into two one-dimensional problems. The results of this study make possible a direct evaluation of this approximation, and of the predictions of various lumped models. It has also been possible to determine the sensitivity of the results to the material and device parameters.

## 6.0 Nuclear Magnetic Resonance in Lead Telluride

Personnel: Professors R. B. Adler, A. C. Smith, S. D. Senturia; M. S. Adler, R. Siegel, J. G. Calderone, C. R. Hewes

Sponsorship: Office of Naval Research, BTL and NSF Fellowships

Our study of the carrier-dependent shifts of the $Pb^{207}$ and $Te^{125}$ nuclear magnetic resonance (NMR) lines in n- and p-type PbTe has continued on several fronts. Measurements on our original pair of samples of the temperature dependence of the shifts between $77^{o}K$ and $470^{o}K$ are complete. These measurements have been made in cooperation with Drs. P. L. Sagalyn and J. A. Hofman of the Army Materials Research Center. An elementary theory based on the changing degeneracy of the carriers with temperature accounts for the observed temporary dependences.

The development of more detailed knowledge of the carrier dependent shifts is being pursued by Mr. Hewes. On the theoretical side, he has written computer programs with which precise comparison between theory and experiment can be made. On the basis of this analysis, we have strong evidence for the importance of a second valence band in lead telluride at temperatures above $250^{o}K$.

The theoretical calculations, however, are sensitive to the precise energy band model used, and currently available experimental data do not permit the determination of a unique set of energy band parameters. We shall, therefore, obtain additional data on the temperature dependences of the carrier dependent shifts in samples which cover a range of carrier concentrations. With such information, we hope to provide new insight into the energy band structure of lead telluride.

Accordingly, we have begun a program of sample preparation and evaluation. We have begun to anneal lead telluride samples in a controlled atmosphere in order to change the carrier concentration, and we now have sufficient facilities and knowledge of the technology to obtain a wide range of n- and p-type samples. The evaluation of the samples consists of measurements of the Hall coefficient and resistivity. The sample evaluation facility includes a phase locked ac measurement system to eliminate thermomagnetic effects and noise inherent in dc measurements.

Progress on our own NMR facility has been such that we can now observe $Pb^{207}$ resonances in PbTe; however, further improvements in sensitivity are still required. We have just obtained an excellent dri free radio receiver which will be the nucleus of a new rf bridge spectrometer now being built by Mr. Siegel. He is also designing a dewar system for arying the sample temperature.

As a corollory to the NMR program in PbTe, we have completed two studies of NMR instrumentation techniques. Mr. M. Adler has carried out an experimental and theoretical study of the operation and sensitivity of transistorized NMR spectrometers. He has also completed the design and construction of a field-tracking NMR gaussmeter. The gaussmeter currently tracks magnetic fields swept over the range 8.0 - 12.5 Kilo-Gauss, and can easily be modified to cover other ranges of field. An account of this work may be found in Mr. Adler's S. M. Thesis, and is being prepared for publication.

Mr. Calderone, in his S. M. Thesis, has carried out a careful study of the sensitivity enhancement achievable in NMR systems by using signal averaging computers.

We have obtained samples of the alloy system $Pb_xSn_{1-x}Te$ for NMR studies to follow the PbTe investigations. The composition and temperature range corresponding to the smallest energy gap should show exaggerated NMR shifts.

Studies have also begun of the ferroelectric system, sodium potassium tantalate. We plan to investigate the quadrupole splittings of the NMR lines as the sample is cooled through the Curie point in order to examine the details of the establishment of long range order.

## 7.0 Cadmium - Zinc Antimonide Solid Solutions

Personnel: Professor A. C. Smith; A. W. Carlson

Sponsorship: National Aeronautics and Space Administration

The current work on this topic has been completed and a technical report issued (see publications). The abstract of the technical report is reproduced below:

Electrical and optical measurements have been made on p-type single-crystal ZnSb, CdSb, and $Cd_xZn_{1-x}Sb$ alloys. For each crystal axis of orthorhombic ZnSb and CdSb, the refractive index, optical absorption, electrical conductivity, and Hall coefficient have been measured. Free-carrier absorption has been identified as the dominant absorption mechanism in the wavelength range of 7 to 15$\mu$. The high-frequency conductivity, observed as free-carrier absorption, and the low-frequency conductivity have been used to uncouple the effective masses and relaxation times. For ZnSb and CdSb the effective mass tensor and relaxation time tensor are calculated from the experimental data. An anisotropic relaxation time is observed for both materials. The optical absorption, electrical conductivity, and Hall coefficient have been meaured for the a and b axes of eight alloy samples. Free-carrier absorption was observed in the alloys and used with the electrical data to obtain the effective masses, $m_a^*$ and $m_b^*$, across the entire alloy composition range. The relaxation-time parameters for the a and b axes are also obtained across the composition range.

## 8.0 Galvanomagnetic Measurements in High-Resistivity Materials

Personnel: Professor A. C. Smith; P. E. Norris

Sponsorship: National Aeronautics and Space Administration

This work has been completed and reported in Mr. Norris' S. M. Thesis. The abstract of the thesis is reproduced below:

The simple theory and phenomenological equations for the Hall Effect are discussed. The limitations of the simple theory are defined for the case of Hall effect and resistivity measurements of insulating semiconductors. Various problems which arise during the measurements of these effects, and techniques for solving them, are examined.

A DC measuring bridge is described which is capable of performing Hall effect and conductivity measurements on samples of up to $10^{15}$ ohm-cm resistance and mobility as low as 1 $cm^2$/volt-second.

Experimental results are given for measurements on Gallium Arsenide. Sources of experimental error are discussed and some suggestions are made for improving the range and sensitivity of the apparatus.

## 9.0 Microelectronics

Personnel: Professor D. Navon; P. Showman

Sponsorship: Advanced Research Projects Agency

Mr. Showman has completed his study of the matching of adjacent silicon monolithic transistors. The measurements indicate a systematic rather than random variation in emitter characteristics across the silicon wafer. Electrical measurements were correlated with the aid of a digital computer in an attempt to isolate the physical cause of parameter variations. The analysis ruled out junction area fluctuations as a cause for mismatch. However, it was not always possible to correlate the variations with a single physical cause, such as impurity concentrations or base width fluctuations. Hypothesizing material "patchiness" offers better correlation possibilities.

## 10.0 Solid State Switching

Personnel: Professors D. Navon, R. D. Thornton; J. Serebrinsky; C. K. Erdelyi, E. A. Miller, S. Spitzer, G. Lichtenberger, P. C. Lindsey, S. Marshall

Sponsorship: U. S. Department of Commerce, Northeast Corridor Transportation Project; National Aeronautics and Space Administration

Professors Thornton and Navon continue work on machinery utilizing kilowatt solid-state commutation. Mr. Erdelyi has completed an unconventional electric motor of high mechanical power output per unit weight. Mr. Marshall is performing motor tests and developing commutation circuitry. Construction of high-power transistors to provide solid-state commutation for this machine were pursued by Messrs. Miller, Lichtenberger, Spitzer and Lindsey. Miller has solved the time-dependent heat-flow equation in typical power transistor structures, leading us to an understanding of the effect of transistor structure design parameters on the instability ("Second Breakdown") problem encountered in semiconductor power devices. Mr. Lichtenberger performed a similar analysis yielding additional information, by solving heat-flow problem using a distributed thermal-circuit analog and subjecting it via the AEDNET computer program.

Mr. Spitzer has measured the thermal instability parameter $\alpha$ for transistors, and has determined a theory for poor high-voltage low-current performance of transistors, compared with their high-current low-voltage behavior. Mr. Lindsey is analyzing the saturation characteristic of power transistors with thick, high-resistivity collector regions needed for high voltage capability.

In another direction, Mr. Serebrinsky has developed and made large area contacts for the high-power transistor designed last year by Mr. P. C. Lindsey. A thin Ni-In-Au "Sandwich" and a careful thermal cycle make it possible to attain the desired goal. The effects of the proposed technology on the device properties are now being evaluated.

## 11.0 Thin-Film Field-Effect Devices

Personnel: Professor D. Navon; R. H. Greischar, J. A. Rome

Sponsorship: Advanced Research Projects Agency

Studies were initiated on thin-film semiconductor materials potentially useful for constructing space-charge limited field-effect transistors. Mr. Rome developed a technique for determining the electrical conductivity tensor for a non-isotropic thin-film material, using evaporated metal contacts which are not necessarily ohmic. The method utilizes four contacts, two measurements, and a tabulation of complex functions (computer generated) for analysis. The method was applied to the study of a thin-film, single-crystal, layered semiconductor-GaSe. Mr. Greischar has vacuum deposited thin-film polycrystalline GaAs onto a quartz substrate. Preliminary I-V measurements indicate space charge limited flow when aluminum electrodes are used.

## 12.0 Study of Basic Device Parameters in the Lead Salts

Personnel: Professors R. H. Rediker, J. Walpole; R. Brodersen, R. Guldi, H. St. Onge

Sponsorship: Office of Naval Research, National Science Foundation Fellowship

The goal of this program is to study in detail some of the physical parameters related to the performance of devices in PbSe. Better understanding and the ability to control or make use of the pertinent properties in PbSe should lead to improvements in existing devices such as lasers and detectors and perhaps to new device applications. An understanding of PbSe should extend to the other lead salts (PbTe and PbS) as well as to the mixed lead and tin salts, due to the similarity of the properties of these materials.

Current projects include studies of lifetime of excess carriers, high-field conduction phenomena and diffused p-n junction diodes. In all three areas of effort, significant variables are the purity of the material and its deviation from stoichiometry, which together determine the carrier concentration. Hence, work on the effects on bulk carrier density and other properties of annealing processes under controlled Se vapor pressure has been undertaken. Material has been produced having hole or electron concentration in the $10^{16}$ and $10^{17} cm^{-3}$ range, and one run yielded p-type material with a concentration of $5 \times 10^{15} cm^{-3}$. Further work will be done to improve the reproducibility of results and to obtain still lower carrier densities. A study of the effects of annealing of foreign impurity content will also be undertaken.

The diffused p-n junctions studied thus far have shown the rather poor reverse voltage-current characteristic common in lead-salt diodes. Devices will now be fabricated using annealed material of lower initial carrier concentration. Brebrick's theory of the inter-diffusion process in binary ionic semiconductors (J. Appl. Phys. 30, 311, (1959)) has been applied to predict the junction profile (spatial dependence of the deviation from stoichiometry) for a limited set of boundary conditions. These results show significant variations in the profile for different diffusion conditions, and they will be extended to include the cases of most practical interest for correlation with diode characteristics and junction capacitances. Results of the studies on lifetime and high-field effects should also increase the understanding of p-n junction properties.

For the lifetime studies, experimental apparatus has been assembled and experiments initiated to observe the luminescence from PbSe optically pumped by a pulsed GaAs laser. The rise and fall times of the luminescence pulse is one means of determining the excess carrier lifetime. The concentration dependence of the lifetime will be investigated.

A study of high-field conduction phenomena in PbSe now seems feasible with material in the $10^{16} cm^{-3}$ or lower concentration range. Equipment for this effort is being obtained and experimental problems such as contacts and heating are being studied.

## 13.0 Photoluminescence from Semiconductors

Personnel: Professors R. H. Rediker, J. S. Moore; A. R. Hartman, W. Berninger, C. R. Grant

Sponsorship: National Aeronautics and Space Administration, Advanced Research Projects Agency, Ford Postdoctoral Fellowship

The goal of this program is the study of photoluminescence in both direct-and indirect-gap semiconductors, and of ways to control this photoluminescence. Equipment is being assembled or built for use in this program. A recording prism spectrometer is now operational and has been used to measure the photoluminescence spectrum of GaAs. system for the deposition of insulating layers using the oxidation of silane has been built, and films of $SiO_2$ have been deposited on Ge, Si, and GaAs. An evaporator for the controlled deposition of nearly transparent metal films has just been put into operation. A tiltable furnace of the type used by Nelson has been built for the liquid epitaxial growth of III-V compounds from saturated solutions in the valence III metal. While the furnace is now being used to grow GaAs from Ga solutions, the program is aimed at the growth of mixed crystals (e.g. $Ga_xIn_{1-x}As$).

In direct-gap semiconductors, field control of the luminescence will be studied. The effort on indirect-gap semiconductors will first concern itself with the photoluminescence from silicon for donor and acceptor concentrations of approximately $10^{16}$ impurities/cm$^3$.

## 14.0 Temperature Dependence of Optically Pumped Semiconductor Lasers

Personnel: Professor R. H. Rediker; H. P. Jenssen

Sponsorship: Advanced Research Projects Agency

The temperature dependence of laser action in optically pumped InAs and InSb has been studied. A GaAs p-n junction laser was used as pump and the laser beam was incident on a cleaved (110) plane of the InAs or InSb. Two other (110) cleaved faces perpendicular to the excited surface formed the laser cavity. The GaAs diode laser was positioned such that a 30-40 $\mu$m wide strip of the full 200 $\mu$m length of the cavity was excited. The GaAs diode laser was operated pulsed with peak output power of 4 watts. Taking into account reflection at the InAs or InSb surface and assuming incident photon generates one hole electron pair, the maximum equivalent current density in the optically pumped laser would then be $2 \times 10^4 A\ cm^{-2}$.

Laser action was observed in an n-type InAs sample ($N_D$ = $2 \times 10^{16} cm^{-3}$) in the temperature range 10 - 40°K. The temperature dependence of the threshold was found to be nearly exponential with threshold increasing from 4 to $10 \times 10^3\ A\ cm^{-2}$ in the range observed. This threshold for optically pumped n-type InAs was significantly higher than that of InAs diode lasers and the temperature dependence of the threshold for the optically pumped lasers was weaker than that of diode lasers. The high threshold in optically pumped InAs could be caused by the lesser degree of mode confinement in optically pumped lasers than in diode lasers. A weaker temperature dependence of the threshold is associated with the higher threshold.

For the three p-type InAs samples studied, threshold was not reached with the available pump power. Since in InAs the split-off valance band is 0.43eV below the topmost valence band and the bandgap is 0.41eV, for p-type material the expected strong reabsorption of the emitted light due to intervalence band transitions could explain the higher threshold.

Laser action was also observed in an n-type InSb sample in the temperature range 8-35°K. The temperature dependence of the threshold was found here to be nearly exponential and increased by a factor of 3 in the range observed. The threshold at 10°K was approximately $6 \times 10^3\ A\ cm^{-2}$.

## 15.0 Electrical and Electro-Optical Properties of Heterojunctions

Personnel: Professor R. H. Rediker; J. Womac

Sponsorship: Advanced Research Projects Agency

Heterojunctions between CdTe and InSb have been fabricated by the interface alloy technique. Laue patterns of the CdTe seed and the regrown InSb were compared and showed that the InSb was single crystal and regrew with the same orientation as the seed. Kossel-line patterns indicate that the junction regions is single crystalline. While n-CdTe to n-InSb junctions do not exhibit rectification, p-CdTe to n-InSb junctions rectify with forward conduction occurring when the p-type CdTe is biased positively. The forward current in the range from $10^{-6}$ amps to $10^{-4}$ amps varied with voltage as exp $\left(\frac{qV}{\eta kT}\right)$ with $\eta \approx 4$ at room temperature and $\eta \approx 30$ at 77°K.

Junctions between InAs and InSb have also been fabricated by the interface alloy technique. Junctions of $p^+$ -InAs to n-InSb have exhibited tunneling at 77°K. Although evidence of InAs optical phonons has been found from measurements of dI/dV and $d^2I/dV^2$ at 4.2°K, no indication of InSb optical phonons has been seen as would be expected if the tunneling were from the InSb valence band to the InAs conduction band. The present results are thus indicative of the typically observed tunneling from bulk $p^+$ -InAs to the $n^+$ inversion layer produced at the surface by metallic contacts.

## Theses

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J. Shah, "An Investigation of AC Electrical Polarization, Photoconductivity, and Optical Charge Transfer in Semi-Insulating GaAs", Ph.D. Thesis, Department of Physics, February 1967.

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S. H. L. Liu, "Equilibrium Junction Potential in Silicon Carbide Diodes With Graded Doping", S. M. Thesis, Department of Electrical Engineering, June 1967.

E. A. Miller, "Analysis of Thermal Instabilities in Power Transistor Structures", S. M. Thesis, Department of Electrical Engineering, June 1967.

P. E. Norris, "Measurement of Galvanomagnetic Effects in High Resistivity Semiconductors", S. M. Thesis, Department of Electrical Engineering, May 1967.

J. A. Rome, "The Conductivity Tensor in Layered Semiconductors", S. M. Thesis, Department of Electrical Engineering, June 1967.

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H. St. Onge, "Electro-Optical Effects in Cadmium Sulfide", S. M. Thesis, Department of Electrical Engineering, June 1967.

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D. C. Green, "A High-Amplitude Current Pulse Generator", S. B. Thesis, Department of Electrical Engineering, May 1967.

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## III. THIN FILM DEVICES

### Personnel

J. E. Ward, Deputy Director, Electronic Systems Laboratory
Professor D. H. Navon, Associate Professor, Electrical Engineering
W. S. Nicol, DSR Staff, Electrical Engineering
R. Greischar, Graduate Student, Electrical Engineering
M. Blaho, Project Technician, Electrical Engineering

### Degrees Granted

R. Greischar, S.M., Electrical Engineering, January 1968.

### Sponsorship

Electronic Systems Laboratory, National Aeronautics and Space Agency, NsG-496(part), DSR 76152T.

### Research Report

#### 1.0 Plasma Oxidized Aluminum Film Studies

Personnel: W. S. Nicol

As part of a continuing study of an evaporated thin film triode, which uses an aluminum grid, some properties of aluminum oxide grown in an oxygen plasma on thin evaporated aluminum films have been investigated. Oxide electric breakdown field strength, growth rate and apparent change in aluminum film thickness during oxidation have been measured. An electron microprobe analysis of reactive sputtering of the plasma electrodes during oxidation has been made in collaboration with Dr. J. Cline, NASA-ERC. The results of this oxide investigation will be applied to the problem of grid insulation in the evaporated triode.

#### 2.0 Evaporated Gallium Arsenide Film Investigation

Personnel: Professor D. H. Navon; W. S. Nicol; R. Greischar

The major emphasis of our thin film work is in an investigation of the structural and electrical properties of two-source evaporated gallium arsenide films.

Several two-source crucible arrangements have been investigated for their suitability in producing uniformly thick films. Film texturing and crystallite size have been examined by transmission and reflection electron microscopy both for amorphous substrates of quartz and for [100] substrates of rocksalt and artificially grown spinel.

For his S.M. thesis, supervised by Professor D. H. Navon, Mr. Greischar has studied the electrical properties of evaporated high resistivity GaAs films and the properties of the metal semiconductor contacts to such films. The films might be characterized by space-charge-limited currents of the form $V^{(T_c + T)/T}$. He has also observed differences in electrical conductance normal to and in the plane of the films which can be explained by a limited contact area mechanism.

Research is now in progress to observe the effect of annealing and doping on the films, using both amorphous and single crystal substrates.

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## IV. CRYSTAL PHYSICS LABORATORY

### Personnel

Professor A. Smakula, Professor, Electrical Engineering
Dr. A. Linz, Research Associate, Electrical Engineering
Dipl. Ing. J. Kalnajs, DSR Staff, Electrical Engineering
Dr. D. Gabbe, DSR Staff (part time), Center for Materials Science and Engineering
Dr. R. Mykolajewycz, DSR Staff, Electrical Engineering
Dr. F. M. Lay, DSR Staff, Electrical Engineering
Dr. F. Martino, DSR Staff, Physics
E. F. Farrell, DSR Staff, Electrical Engineering
V. Belruss, DSR Staff, Electrical Engineering
T. G. Davis, Research Assistant, Electrical Engineering
A. L. Harmer, Research Assistant, Electrical Engineering
B. Chen, Undergraduate, Electrical Engineering
R. S. Karz, Undergraduate, Physics
K. I. Bangerskis, Technical Assistant, Electrical Engineering
A. Vetrovs, Technical Assistant, Electrical Engineering
R. Mills, Technician, Center for Materials Science and Engineering
T. Stewart, Technician, Center for Materials Science and Engineering
Delphine Radcliffe, Secretary, Electrical Engineering

### Personnel who have left during the period

K. I. Bangerskis, Technical Assistant, Electrical Engineering (Now at Kennecott Copper Corporation)
A. L. Harmer, Research Assistant, Electrical Engineering (Now graduate student at Oxford University, England)
Dr. F. M. Lay, DSR Staff, Electrical Engineering (Now at IBM in Kingston, New York)
Dr. F. Martino, DSR Staff, Physics (Now in Quantum Chemistry Group, University of Uppsala, Sweden)
T. Stewart, Technician, (transferred to MIT Department of Metallurgy)

### Degrees Granted

F. Martino, Ph.D., January 1967
A. L. Harmer, S.M., September 1967

B. Chen, B.S., January 1967
R. S. Karz, B.S., June 1967

## Sponsorship

Air Force Cambridge Research Laboratories, AF 19(628)-395, DSR 79166
Advanced Research Projects Agency, SD-90, DSR 75111, 78894
Germanium Research Committee, DSR 79690
Mithras, a division of Sanders Associates, Inc., Sub-contract, DSR 74955, 70757
Office of Naval Research, Nonr-3963(20), DSR 74638
United States Army Engineer Research and Development Laboratories, DA-44-009-AMC-1117(T), DSR 74950

## 1.0 Chemical Preparation of Feed Material

Personnel: Dr. D. Gabbe; K. Bangerskis

Sponsorship: U. S. Army Engineer Research and Development Laboratories, Mithras, a division of Sanders Associates, Inc., and Air Force Cambridge Research Laboratories

### 1.1 Preparation of Cuprous Halides

High-purity CuCl and CuBr have been prepared from commercial reagents by drying in a current of HCl or HBr gas, then zone-refining using 25 passes under a nitrogen atmosphere. The resulting CuCl was colorless and CuBr yellowish; both were fairly transparent in the visible. Attempts to synthesize high purity CuI by this technique were not successful.

### 1.2 Preparation of Fluorides

Techniques have been developed for the chemical purification of rare earth fluorides, $YF_3$, $LiYF_4$, and other fluorides. High-temperature hydrofluorination is used as the final step at present, but work is continuing on high-temperature zone-refining. A temperature controller has been added to the high-temperature zone refiner, and work has concentrated on trying to eliminate contamination from the boat and susceptor materials. Since both tantalum and molybdenum appear to contribute to the contamination, the use of graphite foil shielding and graphite boats is currently being studied.

1.3 Preparation of Thallium Tungstate ($TlWO_4$)

This compound was precipitated from equimolar $TlNO_3$ and $Na_2WO_4$ aqueous solution as a fine powder. Digestion at 90°C overnight yielded hexagonal plates of the compound $Tl_2WO_4$. Some decomposition of the material occurs below its melting point, so this work was not pursued.

2.0 Crystal Growth

Personnel: Professor A. Smakula; Dr. A. Linz, Dr. D. Gabbe; E. Farrell, V. Belruss; A. Vetrovs, K. Bangerskis

Sponsorship: Office of Naval Research, U. S. Army Engineer Research and Development Laboratories, Air Force Cambridge Research Laboratories, Advanced Research Projects Agency, Mithras, a division of Sanders Associates, Inc., Germanium Research Committee

2.1 Growth from Aqueous Solution

2.1.1 Potassium Nitrate ($KNO_3$)

Better control of water bath temperature and stirring has enabled us to grow the crystals on a routine basis as required.

2.2 High-Temperature Solution Growth

2.2.1 Ferroelectric Crystals

A number of the oxide perovskite ferroelectric crystals have been grown by top-seeding, using a solution with an excess of one constituent. Crystals of $BaTiO_3$, $KNbO_3$, $KTaO_3$, $K(NbTa)O_3$, $(K, Na)TaO_3$ were grown as required, either pure or with various dopants.

2.2.2 Complex Germanates

Crystals of $CaGe_2O_5$ were grown with various dopants for fluorescence measurements. This material is orthorhombic and exhibits considerable laminar twinning, making it unsuitable as a laser host material. Other germanates were, therefore, investigated. Large clear crystals of the compounds $Sr_2MgGe_2O_7$ and $Ba_2MgGe_2O_7$ were grown and a charge compensation mechanism using sodium was developed for doping these materials with rare earths. Both of these materials are isomorphous with Akermanite, $Ca_2MgSi_2O_7$. Investigation of techniques for the growth of other complex germanates and silicates is continuing.

#### 2.2.3 Garnets

Small crystals of doped yttrium-iron-garnet are grown as a matter of routine by members of the Microwave and Quantum Magnetics group. The technique used up to now has been the standard one of slow cooling the solution of garnet in a lead oxyfluoride flux. A new top-seeding furnace is being constructed to permit extension of this technique to the magnetic garnet crystals in order to obtain larger sizes and more uniform quality.

### 2.3 Growth from the Melt

#### 2.3.1 Lithium Yttrium Fluoride ($LiYF_4$)

$LiYF_4$ is a scheelite structure fluoride isomorphous with $CaWO_4$. Crystals suitable for laser measurements and doped with varying amounts of neodymium were prepared by a modified Czochralski technique in a high-purity helium atmosphere. The compound is slightly incongruent, so all crystals were pulled from lithium-rich melts. Work on the growth parameters of this material and other complex rare-earth fluorides is continuing.

#### 2.3.2 Rubidium Manganese Fluoride ($RbMnF_3$)

Clear crystals of $RbMnF_3$ are pulled from a melt on a routine basis. Sizes up to one inch in diameter and two inches in length are possible. Some quenching is necessary to eliminate scattering centers completely. A low-temperature fluoride pulling furnace is being reconditioned with a new vacuum system control system in order to meet the demand for fluoride crystals. Further work on reducing the strain in $RbMnF_3$ crystals is in progress.

### 2.3.3 Calcium Tungstate ($CaWO_4$) and other Scheelites

A split cylinder tantalum element resistance furnace has been installed and a series of crystals of $CaWO_4$ doped with Mo and Pb have been grown. The melting temperature of $CaWO_4$ is about 1620°C; consequently the melting is done in a molybdenum crucible under reducing conditions or iridium under oxidizing conditions. The furnace is well suited to sintering studies but less well adapted to crystal growth by the pulling method, due to the sharp thermal gradients and lack of visibility. Consequently a high-temperature RF induction heated furnace has been built and is now in operation. With this furnace, oxides with melting points between 1600°C and 2100°C can be grown under a variety of conditions by the Czochralski technique.

### 2.3.4 Growth by Flame Fusion

The demand for flame fusion crystals has declined somewhat in the last year as new methods became available. A number of crystals of MnO, CoO and NiO, specially oriented, were grown upon request. Use has also been made of the burners to produce amorphous $BaTiO_3$ as a material for a dielectric study.

## 3.0 Crystal Properties

Personnel: Professor A. Smakula; Dr. A. Linz, Dr. R. Mykolajewycz, Dr. F. Lay; J. Kalnajs, E. Farrell, T. Davis, A. Harmer; A. Vetrovs

Sponsorship: Office of Naval Research, Mithras Division of Sanders Associates, Inc., Advanced Research Projects Agency, Air Force Cambridge Research Laboratories, Germanium Research Committee

### 3.1 High-precision Lattice Constant and Density Determination

One of the most direct methods of detecting crystal imperfections is the determination of density from high precision lattice constant measurements, and comparing it with the direct density determined by weighing. Only in a few crystals do both densities agree within two units of the fifth decimal place. In most cases there is already disagreement in the third decimal. Thus the density is very useful for crystal characterization. As an example, the recently determined densities of four crystals are given below.

| Crystal | Lattice Constant a | c | $\rho_x$ | $\rho_w$ |
|---|---|---|---|---|
| $LiYF_4$ (tetragonal) | 5.167 | 10.735 | 3.9816 | 3.9802 |
| $KTaO_3$ (cubic) | 3.989 | - | 7.0123 | 7.0121 |
| CuCl (cubic) | 5.416 | - | 4.138 | 4.137 |
| CuBr (cubic) | 5.691 | - | 5.170 | 5.174 |
| $RbMnF_3$ (cubic) | 4.2405 | - | 4.2974 | 4.2978 |

From the density measurements we can detect crystal imperfections, homogeneity, reproducibility and, in doped crystals, distributions of the dopants, whether substitutional or interstitial.

## 3.2 Thermal Expansion Coefficient

Thermal expansion coefficient measurements are used for the characterization of crystals, particularly in connection with anharmonicity and polarization effects. It would be very desirable to extend such measurements over a wide temperature range. Unfortunately at the present time the measurements are restricted to the range close to room temperature. The expansion coefficients of CuCl and CuBr have been determined by density measurements. The values obtained are:

$$\text{CuCl},\ t = 20 - 30^{o}\text{C},\ \alpha = 13.6 \times 10^{-6}/^{o}\text{C}$$

$$\text{CuBr},\ t = 20 - 30^{o}\text{C},\ \alpha = 15.1 \times 10^{-6}/^{o}\text{C}$$

The older data are unreliable because the samples used were in powder form.

## 3.3 Microhardness of Mixed Crystals

In our general investigation of the physical properties of crystals, the influence of composition on microhardness in mixed crystals has been studied. The hardness of crystals has been related recently to "volumetric lattice energy". It is known that the hardness can be increased by strain or precipitation of impurities. In mixed crystals a certain strain is present because of the difference in atomic size of the components and because of random distribution of atoms. Therefore it is of fundamental and practical importance to know the influence of these effects on the hardness.

The following systems have been studied: KCl-KBr which have NaCl structure, $CaF_2$-$SrF_2$, $SrF_2$-$BaF_2$, both of which have $CaF_2$ structure, and NiO-CoO, which has NaCl structure. In all four systems the hardness has a maximum at 50:50 composition. In systems with very low hardness the increase is quite high (2 - 3 times), but in systems with greater hardness the increase is higher only by a factor of 1.35. The annealing of mixed crystals can reduce the hardness considerably. The microhardness of compounds seems to be equal to the average value of the components.

The microhardness of single crystals depends also on the orientation of the indenter with respect to the crystal orientation. In alkali halides with NaCl structure the greatest hardness on the cubic face is found when the long axis of the indenter is parallel to the cube edge and lowest when it is along the face diagonal. In crystals with CsCl structure the hardness values are just the opposite. Transition metal oxides (MnO, CoO, NiO) behave like CsCl although they have NaCl structure. The change of the hardness with the indenter orientation is related to the plastic deformation of crystals. For a definite correlation we need more experimental results.

## 3.4 Optical Properties

### 3.4.1 Optical Absorption of Single Crystals

Colorless potassium tantalate ($KTaO_3$) is transparent from 0.35 to $4\mu$. Beyond $4\mu$ a series of absorption bands has been observed, superimposed on the continuous absorption increasing toward longer wavelengths. These bands are attributed to overtones and combination frequencies of the fundamental bands which were computed from reflection data using the Kramers-Kronig relation.

Similar infrared bands were detected in mixed crystals of $KTaO_3$-$NaTaO_3$ and in $KTaO_3$-$KNbO_3$, only slightly shifted in their spectral positions.

The ultraviolet and infrared absorption edges of highly purified copper halides have been determined. The CuCl transmits from 0.4 to

$20\mu$ and the CuBr from 0.435 to $30\mu$. The ultraviolet and infrared absorption of $RbMnF_3$ has been measured at 77 and 300°K. There are three strong and four weak bands in the ultraviolet and two weak ones in the visible. Most of the bands split at low temperature. In the infrared $RbMnF_3$ is transparent up to $12\mu$.

The lithium yttrium fluoride shows three absorption bands between 1835 and 2110 A which are probably due to some impurities; in the infrared it is transparent up to $8\mu$.

The two absorption bands at 16 and $18\mu$ observed in mixed crystals of AgCl-AgBr turned out to be caused by some impurities. A highly purified AgBr crystal does not show those bands and is completely transparent from 0.5 to $35\mu$.

### 3.4.2 Absorption Spectra of Hydrogen and Deuterium in $KTaO_3$

The phenomena of chemical reduction in $KTaO_3$ crystals are not well understood. Since reduced $KTaO_3$ is an interesting semiconductor, an investigation was made of the role of interstitial hydrogen ions in this material. Most of the crystals grown in the laboratory show a sharp absorption band at approximately 3470 $cm^{-1}$. This is nearly the same frequency at which OH absorption bands are found in rutile, quartz and other solids. As in rutile, the OH band could be removed by suitable heat treatment or replaced with an OD band at 2567.3 $cm^{-1}$. The reaction is reversible, but the site for the OH or OD appears to be associated with crystal defects, since there is a maximum absorption coefficient which can be obtained for this band for a given crystal, regardless of heat treatment. The strength is variable from crystal to crystal and apparently depends on growth parameters and purity of starting materials.

### 3.4.3 Optical Absorption Spectra of Minerals

Because of the need for new materials to satisfy the host site requirements of such endeavors as laser generation, second harmonic generation in polar host materials, and the intrinsic interest of color effects in complex materials, a study has been made of the optical absorption spectra of some well-known complex silicates.

These include the minerals cordierite and tourmaline, which occur naturally and have a variety of elements such as $Fe^{+2}$, $Fe^{+3}$, and $Mn^{+2}$ as doping agents. Studies of both these materials have been completed in detail. The principal coloring agent has been found to be $Fe^{+2}$ in distorted octahedral symmetry sites. In cordierite this gives rise to a blue color, while in tourmaline the color variations range from pink due to $Mn^{+2}$, to green, blue and black due to $Fe^{+2}$. A brown variety also occurs due to a high amount of $Fe^{+3}$.

Synthesis of these complex silicates with their variable composition may permit tailoring of laser host crystals for specific applications.

### 3.4.4 Fluorescence of Neodymium in Oxide and Fluoride Environments in the Scheelite Structure

Crystals of $LiYF_4$ have been grown doped with .24, 1.4 and 2.2% $Nd^{3+}$. The polarized fluorescence and absorption, excitation spectra, lifetime decay and linewidths have been measured at 77°K and 300°K. The optical data of $LiYF_4:Nd^{3+}$ have been compared with the data of $CaWO_4:Nd^{3+}$.

The spectroscopic features of $LiYF_4:Nd^{3+}$ are: a long lifetime of 500 $\mu$sec, which decreases rapidly with increasing Nd-concentration; a narrow linewidth of 2 $cm^{-1}$ at 77°K; and a high absorption in the near infrared. These factors have been related to its potential as a laser material.

An energy level diagram has been derived for $LiYF_4:Nd^{3+}$ and compared with selection rules. Differences between $LiYF_4:Nd^{3+}$ and other $Nd^{3+}$-doped scheelites have been discussed in terms of different environments of the $Nd^{3+}$ ion in each lattice.

Stimulated emission has been examined in $LiYF_4:Nd^{3+}$. A lightly doped rod containing .24% Nd has a threshold of 4 joules and a slope efficiency of .16% for putput emission at 10,530 A.

### 3.4.5 Optical Fluorescence of $Sm^{3+}$ in $K(Ta,Nb)O_3$ Crystals

The fluorescence spectra of $Eu^{3+}$ and $Sm^{3+}$ ions in crystals of $KTaO_3$ and in mixed crystals of $KTaO_3$-$KNbO_3$(KTN) have been studied. No energy level splittings or fluorescent intensity changes due to the crystallographic transitions are observed. Instead, extra lines appear as the niobium content is increased. The extra lines are possibly due to the distortion caused by the substitution of niobium for tantalum in KTn near the rare earth ion sites. From the ionic size of the activator ions and that of the cations in the host crystals of $KTaO_3$ and KTN, and the comparison of the fluorescent line positions of the $Sm^{3+}$ ions with those in $BaTiO_3$, it is concluded that the $Sm^{3+}$ ions are predominently substituting at the K sites. Some effects of charge compensation and crystal symmetry on the site symmetry for the $Sm^{3+}$ ions in these materials were also noted.

#### 3.4.6 Temperature-dependent Fluorescent Emission in $RbMnF_3$

The absorption, excitation, and emission spectra of $RbMnF_3$ have been studied as a function of temperature. Two weak but broad absorption bands have been observed in the visible, and four strong narrow bands in the ultraviolet, as expected from theoretical considerations. The emission spectrum consists of two bands at 5820 A and 6300 A. Below $20^{\circ}K$ the band at 5820 A predominates. At higher temperatures, up to $90^{\circ}K$, the 6300 A band is strongest. The temperature coefficient of both emission bands is strongly temperature-dependent. Excitation into the visible absorption bands gives the highest yield of emission.

## 3.5 Low Temperature Ferroelectric Transitions

An investigation of the features of ferroelectric transitions at low temperatures (4.2 - $70^{\circ}K$) is being conducted. In order to determine the specific characteristics of low-temperature transitions, the features of a series of mixed crystals having composition-dependent Curie Temperatures are being investigated. The mixed crystals are $(K, Na)TaO_3$; the structure is cubic perovskite above the transition temperature.

The parameters of interest are the temperature and electric-field dependence of the low-frequency transverse-optical lattice vibration mode which gives rise to the ferroelectric transition. This is presently being studied by means of the electric-field induced Raman scattering in the mixed crystals (Fleury and Warlock, Phys. Rev. Letters, April 17, 1967).

## 3.6 Dielectric Properties of Crystals

#### 3.6.1 Dielectric Constant and Loss of LiF at Low Temperature

Using the variational method of Slater and Kirkwood and adopting Landshoff's method for evaluation of the exchange integrals among the non-orthogonal wave functions, Yamashita computed the dielectric constant of LiF for $0^{\circ}K$, $\kappa'_0 = 10.1$. This value was compared with the room temperature value of 9.3. The dielectric constant of LiF at low temperature was not known. We measured the dielectric constant of LiF with frequencies $10^2$ - $10^7$ cps and in the temperature range from $-196^{\circ}C$

to +500°C. As with NaCl, the dielectric constant of LiF increases with temperature in the whole temperature range. At 25°C it has a value of 9.1 and at -195°C a value of 8.45. The extrapolated value to 0°K is 8.4. The discrepancy between the experimental and theoretical value is 20%.

### 3.6.2 Dielectric Constant of CuCl and CuBr

The dielectric data of CuCl and CuBr given in the literature seem to be unreliable. Particularly, the temperature coefficient of dielectric constant given in the literature is about ten times higher than that in other ionic crystals. Since the material is very sensitive to the atmosphere, it is very probable that it was badly contaminated.

Our measurements were taken on highly purified material, using all necessary precautions to prevent contamination. In both materials the dielectric constant at room temperature shows a strong frequency dependence, reaching a constant value at frequencies above $10^5$ cps, as with other imperfect crystals. A great increase of $\kappa'$ with temperature and frequency starts already at -100°C in CuCl and at -50°C in CuBr. At $10^7$ cps the $\kappa'$ at 25°C is for CuCl 8.3 and for CuBr 7.5. The corresponding data for -195°C are 7.3 and 6.9. Since the variation of $\kappa'$ with temperature is not linear, the temperature coefficient varies continuously. Around room temperature, the temperature coefficient of dielectric constant for CuCl is $56 \times 10^{-5}/°C$ and for CuBr $70 \times 10^{-5}/°C$. These are of the same order as in other ionic crystals.

<u>Theses</u>

F. Martino, "Eigenstates of Deep Trap Impurities: The F Center in KCl." Ph.D. Thesis, Department of Electrical Engineering, September 1966.

A. L. Harmer, "Fluorescence of Neodymium in Oxide and Fluoride Environments in the Scheelite Structure," M.S. Thesis, Department of Electrical Engineering, August 1967.

B. Chen, "Electrical Investigation of Doped Potassium Tantalate Crystals," B.S. Thesis, Department of Electrical Engineering, January 1967.

R. S. Karz, "The Conductivity of Carbon Black Dispersions in Polystyrene," B.S. Thesis, Department of Electrical Engineering, June 1967.

## Publications

A. Smakula and J. Kalnajs, "Compelling Evidence of Error in the Atomic Weight of Germanium," Proc Sheve. Sci. Soc. 34, 139 (1967).

A. Smakula, "Invention of Nonreflecting Coating," Kino-Technik, 21, 27 (1967).

A. Smakula, "Defects in Crystal Growth of Transition Metal Oxides," Proc. of International Symposium on Anisotropy in Single Crystal Refractory Compounds, Dayton, Ohio, June 1967.

G. Shirane, B. C. Frazer, V. J. Minkiewicz, J. A. Leake, and A. Linz, "Soft Optic Modes in Barium Titanate," Phys. Rev. Letters, 19, 234 (1967).

E. Farrell and R. Newnham, "Electronic and Vibrational Spectra in Cordierite," Am. Mineralogist 52, 380 (1967).

A. L. Harme A. Linz, D. Gabbe, L. Gillespie, G. M. Janney and E. Sharp, "Fluorescence of $Nd^{3+}$ in YLF ($LiYF_4$)," Bull. Am. Phys. Soc. 12, 1068 (1967).

## Quarterly Progress Reports

Quarterly Progress Report No. 19 covering period December 15, 1966 to March 15, 1967, "A study of the physical properties of high-temperature single crystals," Contract No. AF 19(628)-395.

Quarterly Status Reports Nos. 6, 7, and 8 - "Research on methods of obtaining luminescence in ferroelectric materials and study of the temperature dependence of their luminous efficiencies close to the Curie point," Contract No. DA-44-009-AMC-1117(T) for the inclusive period from October 1, 1966 through June 30, 1967.

Semi-Annual Status Report for period from October 1, 1966, to March 31, 1967 - Growth and Study of Certain Perovskite-Structure and Related Laser Host Crystals. Contract No. Nonr-3963(20).

Semi-Annual Status Report for period from April 1, 1967, to September 30, 1967, - Growth and Study of Certain Perovskite-Structure and Related Laser Host Crystals. Contract No. Nonr-3963(20).

## Final Reports

Final Report on Contract No. AF 19(628)-395 covering period from May 16, 1962 - June 30, 1967 - "A study of the physical properties of high-temperature single crystals".

## V. MICROWAVE AND QUANTUM MAGNETICS GROUP

### Personnel

Professor D. J. Epstein, Professor, Electrical Engineering

Professor F. R. Morgenthaler, Associate Professor, Electrical Engineering

Dr. W. E. Courtney, DSR Staff, Electrical Engineering

D. Bullock, Research Assistant, Electrical Engineering

N. Curland, Research Assistant, Electrical Engineering

H. L. Hu, Research Assistant, Electrical Engineering

Y. S. Lee, Research Assistant, Electrical Engineering

A. Platzker, Research Assistant, Electrical Engineering

S. Rezende, Research Assistant, Electrical Engineering

L. Tocci, Research Assistant, Electrical Engineering

J. Doane, Graduate Student, Electrical Engineering

W. J. Ince, Graduate Student, Electrical Engineering

E. Venturini, Graduate Student, Electrical Engineering

M. Zahn, Graduate Student, Electrical Engineering

D. Fye, Undergraduate Student, Electrical Engineering

M. W. Thomas, Undergraduate Student, Electrical Engineering

Barbara Baldassarre, Secretary, Electrical Engineering

### Personnel who have left during the period

Dr. P. H. Cole, DSR Staff, Electrical Engineering (Now Senior Lecturer in Electrical Engineering at the University of Adelaide, Adelaide, Australia)

Dr. M. A. Wanas, DSR Staff, Electrical Engineering, (Now at Assiut University, Assiut, Egypt)

R. A. Williams, Research Assistant, Electrical Engineering (Now with Fairchild Semiconductor, San Francisco, California)

### Degrees Granted

A. Platzker, S.M., Electrical Engineering, January 1967

H. L. Hu, S.M., Electrical Engineering, June 1967

R. A. Williams, S.M., Electrical Engineering, September 1967

D. Bullock, S.M., Electrical Engineering, September 1967
L. Tocci, E.E., Electrical Engineering, September 1967
L. Kammerdiner, S.B., Electrical Engineering, September 1967
S. Rezende, Ph.D., Electrical Engineering, February 1968

## Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75113
Air Force Cambridge Research Laboratories, Contract AF19(628)-5876, DSR 76282
Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Contract AF 33(615)-3395, DSR 76134

## Research Report

The principal objective of the Group is to clarify and exploit those properties of ferri- and antiferromagnetic insulators which have significance for electronics applications. Professor Epstein and his students have been concerned with studies of magnetic loss mechanisms with a view toward: (1) their control in applications where low loss is an important criterion for design; (2) their utilization where a material must be intentionally absorptive. Professor Morgenthaler and his students have been primarily concerned with microwave magnon/phonon/photon interactions. Interest in this new field of what may be called "microwave magneto-ultrasonics" is warranted because of the fundamental information concerning spin-elastic wave interactions which can be obtained from magnetic and/or ultrasonic spectroscopy and because these interactions make possible novel microwave devices such as magnetoelastic wave parametric amplifiers, tunable delay lines and pulse compression filters.

### 1.0 Magnetic Losses

Personnel: Professor D. J. Epstein; L. Tocci, D. Bullock

### 1.1 Resonance Losses in Garnets

Measurements of the resonance linewidth in silicon doped yttrium-iron garnet (YIG) have been made at 13.5 GHz between room temperature and the Curie point. The linewidth shows a pronounced peak at 105°C.

The anisotropy of the peak, measured in the (110) plane, can be explained in terms of the 4-level valence-exchange model proposed by Clogston. The numerical value for the electron ordering energy extracted from the analysis of the microwave data agrees very closely with what Hunt obtained from his magnetic anneal investigation carried out previously in our laboratory. From the temperature dependence of the linewidth we calculate that the activation energy for electron hopping is 0.25 ev, a value quite close to that found in our conductivity measurements. These resonance studies, which are being made by L. Tocci, will be extended to additional frequencies and to a variety of sample compositions.

The effect of the valence-exchange mechanism on the effective anisotropy fields in Si-YIG is being studied by D. Bullock, who is also reexamining resonance losses previously observed at low temperatures. In these new experiments an attempt is being made to eliminate frozen-in anneal effects by illuminating the sample, thereby stimulating the redistribution of valence-exchange electrons.

## 2.0 Magnetic Domains

Personnel: Professor D. J. Epstein; Dr. M. A. Wanas; H. L. Hu

### 2.1 Domain Wall Motion in Garnets

Our initial studies of domain-wall switching velocity in single crystals of YIG focussed on the role of $Fe^{2+}$ as a "relaxer" ion. Recently, we have studied wall switching as a function of temperature in picture-frame crystals of YIG doped with erbium. The wall mobility results for Er-YIG are quite similar to those for $Fe^{2+}$-YIG. This similarity confirms a previous conclusion, reached on the basis of other evidence, that the switching velocities observed in $Fe^{2+}$-YIG are not controlled by the valence-exchange mechanism.

However, in measurements of wall motion conducted at extremely low excitation levels, valence-exchange does appear to be the dominant loss mechanism in $Fe^{2+}$-YIG. Our conclusion is that in our switching experiments the valence-exchange mechanism is rendered inoperative because the wall traverses its characteristic length in a time short compared with the relaxation time for valence-electron redistribution.

## 2.2 Observation of Domain Patterns

In a recently completed S.M. thesis H. L. Hu has carried out a theoretical investigation of the "signal-to-noise" problems encountered when using the Kerr magneto-optical effect for the observation of magnetic domains. An experimental check on some of the theoretical conclusions is currently being pursued.

## 3.0 Conductivity in Garnets

Personnel: Professor D. J. Epstein; Y. S. Lee

Measurements of Hall effect and conductivity in silicon doped YIG will be made in order to obtain information on carrier concentration and mobility. Hall measurements will be made at temperatures above the Curie point in order to avoid complications arising from the anomalous Hall effect. A high temperature sample holder has been fabricated and is being tested.

## 4.0 Frequency and Mode Conversion of Velocity Modulated Magneto-elastic Waves

Personnel: Professor F. R. Morgenthaler; S. Rezende

The frequency of a magnetoelastic wave propagating in a ferri-magnet can be altered by a suitable time variation of the bias magnetic field, and the character of the wave converted from magnon-like to phonon-like (or vice versa) by suitable time and/or space variation of the bias field; such frequency and/or mode conversion can be utilized in fundamental spectroscopy as well as in the field of microwave ultrasonic devices.

A detailed analysis of the propagation of magnetoelastic waves in spatially uniform, time varying magnetic fields has been carried out, using small signal momentum conservation and coupled mode theory. The magnon/phonon conversion efficiencies have been obtained in terms of critical time gradients of the field. The latter were derived for both shear and longitudinal magnetoelastic waves propagating along principal crystallographic directions. The analysis reveals that for field gradients much less than the critical values, negligible momentum is exchanged between the different branches of the magnetoelastic dispersion relation.

In this case, and as expected, propagation occurs with constant wave-number and momentum, and variable frequency, group velocity, power flow, and pulse duration. Experimental confirmation of these effects in axially magnetized YIG rods has been obtained for the cases when the injected signal is either a magnon (fine wire excitation) or a phonon (piesoelectric excitation). Pulse compression or expansion and change in echo delay time caused by the group-velocity modulation were observed as well. Earlier experimental work involved pulsed frequency conversion of magnetostatic spin waves in an axially magnetized [100] YIG rod in which both upward and downward shifts of from 20-900 MHz were achieved. All of this work will be described in deatil in the Ph. D. thesis of S. Rezende which has also been issued as Technical Report 19.

Currently, the feasibility of practical microwave devices based upon these interactions is being studied.

## 5.0 Phonon-Pumped Magnon Instabilities

Personnel: Professor F. R. Morgenthaler; Dr W. E. Courtney; A. Platzker

### 5.1 Phonon-Pumped Magnons in Ga-YIG

The construction of a phonon-pump spectrometer for operation in the frequency range 0.95 - 1.5 GHz. has been completed. As described previously, the system has been operated in the linear regime over a 400 MHz frequency band centered at 1.2 GHz.

The threshold amplitude for phonon-pumping when the equilibrium position of the magnetization vector is in an arbitrary direction with respect to the crystal axes has been derived. Numerical computations have been made of the threshold phonon power as a function of dc field.

Experiments have been performed with and without magnetic field shaping on a Ga-doped YIG rod with a saturation magnetization of 300 gauss. To increase field homogeneity, the rod was also placed in a sphere of CalVanBIG with similar saturation magnetization. The experimental results are in reasonable agreement with the theory.

### 5.2 Phonon-Pumped Magnons in an Antiferromagnet

Mr. A. Platzker has been carrying out the preliminary phase of his doctoral research involving phonon pumping in $RbMnF_3$. Theoretical studies of phonon-pumped magnons in "flopped" uniaxial antiferromagnets are being extended to cubic antiferromagnets. Preliminary results indicate that the thresholds will be in accord with earlier estimates. New single crystals of $RbMnF_3$ have been grown by the neighboring Crystal Physics Laboratory and cut into oriented rods. The end phases have been ground and polished to optical tolerance and CdS/Al thin film transducers vacuum deposited on them. A computer program is being created to evaluate numerically general phonon pumped spin wave instability thresholds.

## 6.0 Magnetic and Elastic Studies of the Antiferromagnet $RbMnF_3$

Personnel. Professor F. R. Morgenthaler; Drs. P. H. Cole and W. Courtney; W. J. Ince; A. Platzker

### 6.1 Coupled Electronic and Nuclear Modes

Mr. W. J. Ince has carried out a preliminary theoretical investigation of dynamically coupled nuclear electronic spin resonance of $Mn^{2+}$ in $RbMnF_3$. The theory differs from that of previous investigations, which assumed that the nuclear spins are unable to follow the precessional motion of the electrons. In general, the complexity of the dynamically coupled resonance analysis is only warranted if the electronic and nuclear normal mode frequencies are close. However, in $RbMnF_3$ it is shown that there is significant deviation in the frequencies calculated by the two approaches for certain crystal orientations and field strengths. Greatest deviation occurs when the magnetizing field is parallel to a [100] direction and when the spins are almost flopped.

A coaxial resonator, capable of being tuned over a very broad frequency range, is under construction. With the use of field modulation both nuclear and electronic modes should be observable over the temperature range 4.2°K to 77°K.

Double resonance has been observed in $RbMnF_3$ at 4.2°K. The sample was mounted in an X Band $TE_{101}$ cavity, having a resonant frequency of 10.24 GHz. The UHF pump and X Band fields were mutually orthogonal, but tilted 45° with respect to the steady field. In this manner a shift in both the tunable and field independent AFMR resonances was detected.

## 6.2 Nonlinear Effects in Antiferromagnetic Resonance

The general aim of this research has been the study of spin wave relaxation in $RbMnF_3$ through examination of nonlinear processes of various orders which couple uniform mode and spin wave magnons. The first avenue of approach used for the study of nonlinear processes followed the saturation of resonance susceptibility experiments carried out by Heeger on the related material $KMnF_3$. The experiments performed here on $RbMnF_3$ extended the input power level to 20 db above the critical power in order to study in detail the tail of the decline of susceptibility curve.

The interpretation of these experiments in terms of a variety of models has been investigated. The existing analyses for the instability threshold, which do not apply to the common experimental situations, were extended to include an arbitrary from of anisotropy surface in the flopped configuration. The experimental results, which include measurements of low power resonance linewidth and high power instability threshold, show the uniform sample concept to be clearly inadequate. An alternative but unsophisticated theory which assumes the sample to be composed of uncoupled regions of varying characteristics can be made to fit the observations by a suitable adjustment of material parameters. A more refined version of this theory, which assumes a random variation of anisotropy field (possibly of strain origin as suggested by Eastman) with a certain autocorrelation distance has been prepared. When the autocorrelation distance exceeds a certain quite small value, some simplifications in the theory are possible and permit a simple comparison with experiment. The experiments have been interpreted successfully along these lines. It is interesting to note that the magnitude of the autocorrelation distance is not provided by experiments of this nature. Possibly experiments involving optical scattering from antiferromagnetic magnons can be carried out and may allow determination of this distance. A second set of nonlinear phenomena used for studies of this material are those which connect harmonically related modes of resonance that exist in certain situations in cubic antiferromagnets when the easy axis lies along the body diagonals. The details of this research are described in Microwave and Quantum Magnetics Group Technical Report 9.

## 7.0 Exchange Torque, Power and Momentum Flow, and Stress in a Rigid Ferrimagnet

Personnel: Professor F. R. Morgenthaler

A self-consistent formulation of the exchange energy density, effective exchange field, and Poynting vector previously carried out for a rigid ferrimagnet has been extended to the case of a deformable medium with general magnetoelastic coupling.

Small signal equations of motion governing the elastic displacement and sublattice magnetization vectors in a magnetoelastic ferrimagnet were used to formulate conservation laws that allow identification of the small signal power, energy, stress, and momentum. These quantities include contributions from the electromagnetic, Zeeman, exchange, anisotropy, elastic, and magnetoelastic fields. Both time-dependent and complex forms of the power theorem have been derived and a time-and space-dependent stress-momentum theorem given for a medium with spatially uniform equilibrium parameters. The small signal torque density and power flow vectors were used to deduce self-consistent boundary conditions that connect the values of the small signal fields on the two sides of a surface of passive discontinuity. These results were in turn employed to generalize the stress tensor so that its components remain finite in a medium with spatially nonuniform equilibrium parameters. In this case, nonconservation of stress-momentum occurs and leads to the existence of a nonzero small signal force density. The general time- and space-dependent equations were also used to derive approximate equations of motion governing localized wave packets described in terms of quasiparticles. The results have been specialized to the cases of a ferromagnet and an antiferromagnet. On the basis of the work, calculations of magnon trajectories are being carried out for both the microwave and exchange bands. Exchange-band magnons are of interest because with respect to the microwave branch magnons their effective mass is of the opposite sign.

## 8.0 Direct Coupling of Magnetoelastic and Electromagnetic Waves at a Material Interface

Personnel: Professor F. R. Morgenthaler; J. Doane

Coupling between photons, magnons, and phonons caused by an abrupt discontinuity in the material parameters of a magnetoelastic ferromagnet has been considered. The simultaneous presence of evanescent and propagating waves can, under suitable circumstances, lead to direct transfer of power between the electromagnetic, exchange, and elastic channels. As an example, the partial conversion to spin wave of a circularly polarized electromagnetic wave, traveling in air and normally incident upon a ferromagnet, has been analyzed in detail for the case when the material is uniformly magnetized to saturation along the direction of propagation. The effects of anisotropy, oblique angles of incidence, and multiple discontinuities are currently being studied.

## Theses

S. M. Rezende, "Magnetoelastic and Magnetostatic Waves in Time-Varying Magnetic Fields", Ph.D. Thesis, Department of Electrical Engineering, February 1968.

D. C. Bullock, "The Frequency Dependence of Anisotropy Fields in Silicon-Doped Yttrium-Iron Garnet", S.M. Thesis, Department of Electrical Engineering, August 1967.

H. L. Hu, "Study of Domain Structures Using Kerr Magneto-Optics", S.M. Thesis, Department of Electrical Engineering, May 1967.

A. Platzker, "Magnetoelastic Properties of YIG as a Function of Temperature", S.M. Thesis, Department of Electrical Engineering, January 1967.

L. R. Tocci, "Measurement of Ferrimagnetic Linewidth", E.E. Thesis, Department of Electrical Engineering, August 1967.

R. A. Silliams, "Magnetic Anisotropy Measurements on Silicon-and Gallium-Doped YIG", S.M. Thesis, Department of Electrical Engineering, June 1967.

L. Kammerdiner, "Magnetostatic Spin Wave Propagation in Ferrites", S.B. Thesis, Department of Electrical Engineering, September 1967.

## Publications

P. H. Cole, "Antiferromagnetic Spin Wave Instability Calculations in the Flopped State", Electronics Letters <u>3</u>, 363 (1967).

P. H. Cole, "Nonlinear Coupling Between Antiferromagnetic Resonance Modes in $RbMnF_3$", Appl. Phys. Letters <u>10</u>, 272 (1967).

P. H. Cole and W. E. Courtney, "Uniform Mode Resonance and Spin Wave Instability in $RbMnF_3$", J. Appl. Phys. 38, 1278 (1967).

D. E. Eastman, "Ultrasonic Study of First-Order and Second-Order Magnetoelastic Properties of Yttrium-Iron Garnet", Phys. Rev. 148, 530 (1966).

D. J. Epstein and L. R. Tocci, "High Temperature Resonance Losses in Silicon Doped Yttrium-Iron Garnet (YIG)", Appl. Phys. Letters 11, 55 (1967).

D. J. Epstein, "A Thermodynamic Treatment of Penfield's Paradox in Circuit Theory", Proc. IEEE 55, 2173 (1967).

C. P. Hartwig, "Suppression of Spin-Wave Instabilities by Field Modulation", J. Appl. Phys. 38, 1220 (1967).

R. P. Hunt, "Magnetic Annealing Effects in Silicon-Doped Garnets", J. Appl. Phys. 38, 2826 (1967).

F. R. Morgenthaler, "Exchange Energy, Stress and Momentum in a Rigid Ferrimagnet", J. Appl. Phys. 38, 1069 (1967).

F. R. Morgenthaler, "Photon/Magnon Conversion Near a Material Interface", Electronics Letters 3, 299 (1967).

S. M. Rezende and F. R. Morgenthaler, "Frequency Conversion of Spin Waves in Pulsed Magnetic Fields", Appl. Phys. Letters 10, 184 (1967).

S M. Rezende and F. R. Morgenthaler, "Magnetoelastic Waves in Pulsed Magnetic Fields", Appl. Phys. Letters 11, 24 (1967).

D. I. Tchernev, "Effect of Low Temperature Magnetic Anneal on the Linewidth of Garnets Containing $Fe^{2+}$ Ions", J. Appl. Phys. 38, 1046 (1967).

M. Wanas, "Domain-Wall Motion in Yttrium-Iron Garnets", J. Appl. Phys. 38, 1019 (1967).

## Papers Presented at Meetings

The following papers were presented at the 1967 Ultrasonics Symposium held October 4-6 in Vancouver, B.C.:

W. E. Courtney and F. R. Morgenthaler, "Instability Thresholds for Phonon-Pumping in a Cubic Ferromagnet".

F. R. Morgenthaler, "Small Signal Conversation Theorems and Boundary Conditions for a Magnetoelastic Ferrimagnet".

F. R. Morgenthaler, "Direct Coupling Between Photons, Magnons and Phonons at a Material Interface".

S. M. Rezende and F. R. Morgenthaler, "Magnetoelastic Wave Propagation in Time Varying Magnetic Fields".

Technical Reports

A. Platzker, "Magnetoelastic Properties of YIG as a Function of Temperature", Technical Report 12, MIT, Cambridge, Mass., January 1967.

P. H. Cole, "Magnetoelastic Parallel-Pump Instabilities for Generally Directed Waves", Technical Report 13, MIT, Cambridge, Mass., April 1967.

F. R. Morgenthaler, "Small Signal Power and Momentum Theorems for a Magnetoelastic Ferromagnet", Technical Report 14, MIT, Cambridge, Mass., May 1967.

S. M. Rezende, "Magnetoelastic Waves in Pulsed Magnetic Fields", Technical Report 15, MIT, Cambridge, Mass., June 1967.

W. E. Courtney, "Instability Thresholds for Phonon-Pumping in a Cubic Ferromagnet", Technical Report 16, MIT, Cambridge, Mass., May 1967.

D. J. Epstein and L. R. Tocci, "High Temperature Resonance Losses in Silicon Doped Yttrium-Iron Garnet (YIG)", Technical Report 17, MIT, Cambridge, Mass., June 1967.

P. H. Cole, "Second Order Coupling by Anisotropy and Exchange in Antiferromagnetic Resonance", Technical Report 18, MIT, Cambridge, Mass., June 1967.

S. M. Rezende, "Magnetoelastic and Magnetostatic Waves in Time-Varying Magnetic Fields, Technical Report 19, MIT, Cambridge, Mass., December 1967.

# VI. PARTICLE OPTICS LABORATORY

## Personnel

Professor C. K. Crawford, Assistant Professor, Electrical Engineering
K. L. Wang, Graduate Student, Electrical Engineering
M. D. Brody, Graduate Student, Electrical Engineering
A. A. Langer, Undergraduate Student, Electrical Engineering
S. M. Rose, Undergraduate Student, Electrical Engineering
G. S. Solomon, Undergraduate Student, Electrical Engineering
H. Wilhelmsen, Undergraduate Student, Electrical Engineering
D. K. Owens, Undergraduate Student, Physics
N. D. Punsky, Undergraduate Student, Electrical Engineering
Susan Greiner, Secretary, Electrical Engineering

## Degrees Granted

M. D. Brody, S.M., Electrical Engineering, September 1967
A. A. Langer, S.B., Electrical Engineering, June 1967
S. M. Rose, S.B., Electrical Engineering, June 1967
G. S. Solomon, S.B., Electrical Engineering, June 1967

## Sponsorship

Air Force Materials Laboratory, F33615-68-C-1020, DSR 70653
NASA Electronics Research Center, NAS12-558, DSR 70444

## Research Report

This laboratory was set up to study low energy charged particle optics, neutral and charged particle beams, and related fields.

### 1.0 Electron Ionization Cross Sections

Work is continuing on the measurement of electron ionization cross sections using a large quadrupole mass spectrometer. A new technique for measuring cross sections which uses two electron-impact ionization chambers stacked in series on a single atomic beam is being perfected.

The first chamber modulates the beam while the second chamber detects this modulation, thus allowing the simultaneous absolute determination of the cross section and the number density in the beam. The technique is potentially powerful since, when combined with the mass spectrometer, it would allow the instantaneous measurement of cross sections and flow rates in a fluctuating multicomponent atomic beam.

Cross sections for single and double ionization of metal vapors, obtained by an atomic-beam-trap weight-gain method, are being published.

A new ultra-high vacuum system has been set up and is in use studying space charge neutralization in electron ionization chambers.

A program has been initiated to develop high-intensity atomic-beam sources which are free of charged particles. The major sources of these unwanted particles are: the Knudsen-cell bombardment-heating electrons generating ions from background gas, the bombardment electrons themselves, the emission of ions from hot surfaces by surface ionization, and the emission of Auger electrons from electrode surfaces bombarded by ions. By use of various suppression electrodes, it is possible to obtain neutral beams with all of these effects suppressed to below $10^{-10}$ amps; further improvement is expected.

## 2.0 Ion Implantation Fabrication of Semiconductor Devices

Another project is under way designing ion sources suitable for the ion implantation fabrication of semiconductor devices. There is a need for sources which are stable, compact, reliable, require little power, which produce ions only of the desired species, and which can be simply switched from element to element. Ion sources which are to be used to implant by image optics (to make very large numbers of components in one simultaneous operation and to reduce their size) must have high intrinsic brightness and a narrow energy spread. One promising idea appears to be the use of ions from the plasma produced by the impact of a laser beam on a solid. Problems to be solved include space-charge spreading, recombination within the plasma, and the perveance limit of the extraction geometry.

## 3.0 Electron and Ion Beam Testing of Microcircuitry

A program has been set up to explore the feasibility of using small diameter electron and ion beams as current sources to test microcircuits. These beams would be focused on small circular contact pads built into the microcircuits, which could be much smaller than the test pads presently contacted by mechanical probes. Problems concerning stability, secondary emission, intrinsic brightness, and methods of injecting positive currents, are being considered.

## 4.0 Construction Techniques

Small, rugged, low cost thermal manipulators have been developed for use in ultra-high vacuum. When driven by a simple feedback loop using a thermocouple position sensor, they can provide accurate positioning along with response times of less than one second. A theoretical analysis was conducted concurrently with the fabrication of the manipulators, however, and it was shown from thermodynamic considerations that the work output (for reasonable input energy) is limited by the nature of the working substance, is fundamentally low, and that there is little hope of achieving significant improvement. Thus the manipulators are useful only in applications where small forces are required, such as scanning a beam, orienting a sample, or moving a shutter. One of the manipulators is now in use running a shutter on our cross section measuring apparatus.

### Theses

M. D. Brody, "Crossed Beam Ionization Chamber Charge Neutralization," S.M. Thesis, Department of Electrical Engineering, September 1967.

A. A. Langer, "High Brightness Beams from Low Temperature Cathodes," S.B. Thesis, Department of Electrical Engineering, June 1967.

S. M. Rose, "A Stabilized Evaporator for the Metals Tungsten, Tantalum and Molybdenum," S.B. Thesis, Department of Electrical Engineering, May 1967.

G. S. Solomon, "The Production of High Intensity Molecular Beams," S.B. Thesis, Department of Electrical Engineering, June 1967.

### Publications

C. K. Crawford, "Design of Thermal Manipulators for Ultra-high Vacuum", J. Vacuum Science and Technology, in press.

C. K. Crawford and K. L. Wang, "Electron-Impact Ionization Cross Sections for Silver", J. Chem. Phys., in press.

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# SECTION C

# METALLURGY AND MATERIALS SCIENCE

## I. PHYSICS OF SOLIDS

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Dr. B. Golding, Research Associate

Degrees Granted

T. A. Rowe, S.M., Metallurgy, June 1967
J. E. Woodilla, Sc.D., Metallurgy, June 1967

Sponsorship

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Advanced Research Projects Agency, SD-90, DSR 75123, 75125, 78897
Office of Naval Research (Project MAC) Nonr-4102(01), DSR 79457
U. S. Air Force - Wright Air Development Center, F33615-67-C-1226, DSR 70321
United States Steel Corporation, DSR 70216
Xerox Corporation, DSR 74997

Research Report

Introduction

The object of much of the research in the Physics of Solids group is the development of a quantitative understanding of some of the more complex forms of condensed matter. For example, electron states are studied in binary alloy systems as opposed to the simpler pure materials, and the structures and properties of liquids, amorphous materials, and alloys are studied in addition to the perfectly periodic solid.

The general areas of research interest are the scattering of electrons, neutrons, and x-rays from solids and liquids; the electronic structure of metals, alloys, and molecules; order-disorder phenomena; ultrasonic properties of solids; and the study of local environments in solids. Research programs in these areas are described in detail in the following sections.

1.0 Spin Correlations in Magnetic Materials

Personnel: Professor B. L. Averbach; K. R. Morash, M. D. Rechtin, R. S. Shemenski

Sponsorship: National Science Foundation, NSF GP-5463, DSR 76275

The arrangement of spins in ferromagnetic and antiferromagnetic materials is being investigated by means of neutron scattering observations. Work here has shown that there is considerable short range order above the critical temperature and the local arrangement of spins is being investigated at temperatures above and below the magnetic transition. Detailed studies are being made in single crystals of MnO, CoO, and NiO well above the Neel temperature. It appears that antiphase domains exist well above the critical temperature and these domains frequently form well-defined modulated spin structures. These spin waves change as the critical temperature is approached and the development of long range order from these modulated structures is being investigated.

Spin correlations are also being measured in Fe-Si, Fe-Al and in Fe-Ni single crystals. The magnetic properties of these materials are being measured, and attempts are being made to correlate the magnetic parameters with the spin arrangements.

2.0 Atomic Arrangements in Selenium

Personnel: Professors R. Kaplow, B. L. Averbach

Sponsorship: Xerox Corporation, DSR 74997

A study is being made of the structure of vitreous and crystalline selenium. X-ray diffraction data at 25 and -196°C have been used to obtain radial distribution functions for amorphous and hexagonal selenium. The amorphous selenium exhibits strong correlation peaks at 2.43, 3.75, 5.8, 7.2 and 9.3 A. The first two distances are observed in both the hexagonal form, which consists of spiral chains, and the monoclinic form, which consists of eight-membered puckered rings. The remaining major peaks do not correspond to intramolecular distances in any of the crystalline forms. Attempts have been made to match the experimental amorphous distribution function with models which involve perturbations of the atom positions in the hexagonal and in the monoclinic crystalline forms. A computer array consisting of 100 atom positions is used and perturbations are chosen by a Monte Carlo procedure which allows only those perturbations which improve the fit to the experimental distribution function. It has been shown that relatively small static displacements are sufficient to convert the monoclinic ring structures to the observed vitreous form. Much larger perturbations are required to convert the hexagonal chain structure into a form which provides a suitable amorphous radial distribution function. It is concluded that vitreous selenium at room temperature probably consists mostly of slightly distorted rings along with some atoms whose local symmetry is like that in the chains. Such a structure appears to be consistent with recent infrared and Raman data.

The Monte Carlo simulation of the amorphous structure is being improved and these techniques are being applied to the study of selenium-arsenic alloy and to other vitreous material.

## 3.0 Ultrasonics at Phase Transitions

Personnel: Professor S. C. Moss; Dr. B. Golding

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75125

Extensive finely spaced data have been collected on the variation of ultrasonic velocity and attenuation in the vicinity of the Neel temperature (approximately 83$^{\circ}$K) of the cubic Heisenberg antiferromagnet $RbMnF_3$. The frequency dependence of these properties has been measured and the results indicate two distinct regions of interest:

(a) The critical point where critical-like behavior is observed in both the compressibility and attenuation.

(b) Below the critical temperature where the frequency dependence of the attenuation indicates the possible influence of domain walls.

The ultrasonic attenuation coefficient $\alpha$ is divergent at $T_c$ and obeys the law: $\alpha \propto \omega^2 (T - T_c)^{-.32 \pm .02}$ for two decades of reduced temperature, $T/T_c - 1$.

## 4.0 Theoretical Electronic Structure of Materials

Personnel: Professor K. H. Johnson

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75123

The nature of this research program is the calculation from first principles of the electronic energy levels and wave functions for a variety of materials, with the object of relating the results to observed electronic and other physical properties. Current projected research fall into three general areas:

(a) The calculation of electronic energy bands and Fermi surfaces of ordered metallic compounds by the KKR or Green's function method. Computations can be carried out using both a constant wave vector search and a constant energy search. Working computer programs also permit the calculation of relativistic and magnetic effects, and are applicable to crystals with several atoms per unit cell. Extensions of the programs to include self-consistency are planned. Applications are currently being made to alloys such as $\beta'$AgZn and $AuAl_2$ for which reliable experimental Fermi-surface data is available. The theoretical results are also being used to discuss the relationship between electron concentration and alloy phase stability.

(b) Theoretical studies of the electronic structure associated with impurities in crystals. A "multiple-scattering" or Green's function model is being developed for the approximate calculation of the localized electronic configurations associated with impurities and the effects of impurities on the band structure, density of states, and Fermi surface of the solvent crystal. The model has the advantage over other methods that one can compute with relative ease the effects due to clustering of impurities and lattice distortion, while being applicable to all classes of crystals and impurities, including transition and magnetic metals. A study of the relationship between this approach and the one-electron theory of non-dilute disordered alloys is also being made.

(c) The calculation of the one-electron eigenstates associated with polyatomic molecules and macromolecules of biological interest. A Green's function technique has been developed for the approximate determination of the electronic structures of complex molecular systems. The computational simplicity and applicability of this method to molecules of arbitrary sterochemical structure are dependent on the adoption of a model Hartree-Fock Hamiltonian similar to that used in energy-band calculations for crystals.

The method is of particular advantage in treating large polyatomic systems where more conventional molecular-orbital techniques are difficult to apply. Projected applications include molecular complexes such as the sulfate ion and the metal porphyrins, which are significant to biology. The method can also be applied to determinations of both the localized electronic structure and the energy bands of periodic, quasi-periodic and aperiodic macromolecular systems; e.g., molecular crystals, polymers, and helical systems important to biology (proteins, DNA, etc.).

## 5.0 Fermi Surfaces of Ordered Alloys

Personnel: Professor D. J. Sellmyer; J. Ahn

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75123

Measurements are being made on the Fermi surfaces of a number of ordered alloys and metallic compounds having several of the simpler crystal structures. The results are being combined when possible with the type of realistic energy band calculations which are beginning to emerge for these types of metals. The object of the work is a quantitative understanding of the electronic structure and quantum chemistry of this class of materials. The experimental work is done at the National Magnet Laboratory in fields up to 150,000 gauss. Systems being studied include:

(a) $\beta'$-CuZn (CsCl structure). We have completed a detailed study of the high-field magnetoresistance of $\beta'$-CuZn. The results indicate that it is an uncompensated metal and that its Fermi surface is multiply connected. Strong open orbits were observed when the field was in $\{110\}$ or $\{100\}$ planes and this behavior is compatible with the Fermi surface model predicted by augmented-plane-wave and Green's function energy band calculations. There are certain aspects of the data which cannot be explained in terms of the theoretical model unless some of its dimensions are changed and unless open orbits due to magnetic breakdown are taken into account.

(b) $AuX_2$ where X = Al, Ga, In (fluorite structure). The magnetoresistance of these compounds has been measured and compared with the predictions of a nearly free electron model assuming seven conduction electrons per primitive cell. In general there is qualitative agreement except for one field direction where magnetic breakdown is suspected. Measurements of the Hall coefficient are being made to try to resolve this problem.

(c) AuSn (NiAs structure). High-field magnetoresistance measurements indicate that the Fermi surface of AuSn supports open orbits in [0001], <1010>, and <1120> directions. Cross-sectional areas of the Fermi surface have been measured with the Shubnikov-deHaas effect but the amplitude of the oscillations is large enough to be observed only when the field is in the basal plane. Three sets of frequencies were observed and the results are being compared with the single-OPW Fermi surface model.

(d) $AuSb_2$ (pyrite structure). A very high purity single crystal (resistance ratio ~600) has been grown. Preliminary magnetoresistance measurements have been made and deHaas-van Alphen work is planned.

## 6.0 Electronic Structure of Dilute Alloys

Personnel: Professors D. J. Sellmyer, B. L. Averbach; I. S. Goldstein, P. J. Tobin

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75123

We are studying changes induced in the Fermi surfaces of pure metals upon dilute alloying. The field-modulation method of observing the deHaas-van Alphen effect is being employed. Cross-sectional areas of the third-zone Fermi surface of PbIn alloys have been measured, for concentrations ranging from 0 to 0.6 atomic per cent indium. The measurements will be extended in concentration as far as possible and the results compared with the theories of electronic states in dilute alloy systems.

## 7.0 The Effect of Pressure on the Elastic Constants of Beryllium and Beryllium Alloys

Personnel: Professor B. L. Averbach; D. J. Silversmith

Sponsorship: U. S. Air Force Wright Air Development Center, F33615-67-C-1226, DSR 70321

The elastic constants of beryllium and beryllium-copper alloys are being determined by an ultrasonic technique as a function of hydrostatic pressure. The changes in elastic anisotropy are being investigated as a function of pressure and alloy content, and it is expected that these data will provide some insight into the reasons for the unusual axial ratio of the beryllium unit cell. It is also anticipated that these data will provide a picture of the electron distribution in the outer regions of the atom and thus lead to a better understanding of the physical properties of beryllium.

## 8.0 Inelastic X-ray Scattering from Beryllium and Beryllium Alloys

Personnel: Professors R. Kaplow, B. L. Averbach; R. Currat

Sponsorship: Wright Air Development Center, F33615-67-C-1226, DSR 70321

The properties of a given material are largely determined by the characterisitc spatial and momentum distribution of its electrons. It is possible to calculate electronic band structures with various approximate methods and there are various experimental techniques which allow measurement of certain aspects of the electronic structure. In particular, measurement of the energy and angular distribution of scattered x-rays can yield both the spatial and momentum probability densities. We are presently concentrating on measurement of the inelastic components of the scattering from pure beryllium, repeating experiments which have recently been completed elsewhere, and hope to extend such measurements to beryllium alloys.

The experimental arrangement utilizes a line-focus molybdenum target x-ray tube, with two crossed ± $3^{\circ}$ molybdenum soller slits between the tube focal spot and the specimen. Radiation scattered at a variable angle from the specimen is energy-analyzed using the (400) reflection of a ground and bent LiF crystal analyzer, mounted on the central post of a diffractometer. Data is obtained by rotating the analyzer crystal and detector, in the usual manner, over an angular region sufficient to include the energy range of interest. The data is recorded in a 1024 channel multiscalar, whose channels are commutator-synchronized to the diffractometer; a complete data set represents many successive passes over the required angular region with fast reversal of the diffractometer and triggering of the multiscalar being controlled automatically. Thus the inherently low counting rates which are commensurate with fine resolution can be utilized without introducing a sensitivity to slow variations of the x-ray supply.

## 9.0 Low Angle Scattering of X-rays

Personnel: Professors S. C. Moss, J. Cahn; J. Kitler

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75125

The Kratky camera is currently being used to study phase separation (or spinodal decomposition) in initially single phase multicomponent glass systems. The kinetics of the process will be studied in detail and compared with the theory of Cahn.

Some limited work is also beginning on density fluctuations in polymer films.

10.0 Atomic Arrangements in Interstitial Phases

Personnel: Professor S. C. Moss; J. Zagarins

Sponsorship: United States Steel Corporation, DSR 70216

(Research performed in cooperation with Professor M. Cohen)

Work is underway on an investigation of the interstitial solution of oxygen in zirconium. Several single crystals are being prepared and will be diffused with oxygen to various levels up to the solubility limit of approximately 30 at. % 0. Studies will be made to determine:

(a) The change in elastic properties with oxygen addition; i.e., lattice dynamical effects of interstitial alloying.
(b) The degree of lattice distortion produced by the oxygen interstitials - an x-ray study.
(c) The degree to which the oxygen atoms are in ordered sites within the zirconium lattice - an x-ray study to examine the possibility of an order-disorder transition.

Both Zr-O and Ti-O solutions exhibit a maximum in the liquidus at exactly 25% 0 with congruent melting at this point. The alloys also exhibit unusual plastic behavior with increasing oxygen content and this investigation is an attempt to understand some of these properties in terms of the structure of solutions.

11.0 On Line Systems for Numerical Analysis

Personnel: Professor R. Kaplow; Dr. J. Brackett

Sponsorship: Project MAC, DSR 79457 and Advanced Research Projects Agency, SD-90, DSR 78897

MAP, developed for use within the MIT time-sharing computer system (CTSS), has proven its usefulness in a large number of research and teaching applications, in spite of its inherent inefficiencies. It includes the facilities for handling one-dimensional problems in equation format, with the additional capabilities of various specialized operators such as integrations, Fourier transforms, convolutions and correlations, change of variable, interpolation, etc., as well as a full package of matrix operators. In addition to flexible input and output via the console typewriter, output commands allow displays on the available refresh-type or storage-type oscilloscope display units. Since CTSS is scheduled to be closed out shortly, recent efforts have been directed towards a new system, rather than improving the efficiency and scope of the present system. In this effort we will likely be cooperating with a group at Bell Telephone Laboratories (Whippany).

The complete specifications for the new system, even in their initial and tentative form, are far too numerous to list here. It is fairly certain however (a) that the available classes of data entities will be enlarged to include two- and three-dimensional "functions" of specifiable independent variables, as well as three-dimensional arrays; (b) that there will be generalized, multiparameter operators which will be able to appear directly in the equation format; (c) that the present "command sequence" concept will be broadened to include flexibility regarding the definition of local variables; and (d) that it will be possible to retain the symbolic definition of data entities, perhaps for subsequent symbolic manipulation.

## 12.0 A Teacher-oriented System for Writing Teaching Programs

Personnel: Professor R. Kaplow; Dr. J. Brackett, D. Hall

The major difficulties regarding the broad application of on-line digital computers to problems of education, in particular through so-called computer-aided-instructions, are the relative sophistication in the computer arts and the obligation of considerable time required of the teacher. We are, therefore, now approaching this problem directly from the point of view of the teacher, and are developing a teacher-interactive system, which will require no programming ability from the teacher and which will, moreover, simplify for him the process of developing a logical and self-consistent tutorial session; on completion of the teacher's specification of the desired student interaction, a suitable program will be generated automatically.

## 13.0 Transport Properties and Magnetism in Alloys

Personnel: Professor D. J. Sellmyer; G. Caskey

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75123

Thermoelectric power, resistivity, and susceptibility measurements are being made in the alloy systems FeAl, CoAl, and NiAl near and at the equiatomic composition. The temperature range of the measurements is $1^{\circ}$K to $300^{\circ}$K. These materials have the CsCl structure at the equatomic composition. The object of this work is therefore: (a) to try to determine the extent to which their electronic structure and properties can be understood in terms of the electron compound ideas which seem to work for the nontransition metal alloys of the same structure, and (b) to study the magnetic behavior of systems which should be simple enough to be handled theoretically, for example, with the unrestricted Hartree-Fock method.

In addition, sample preparation work has begun with the aim of investigating the formation of localized moments in normal metals with small amounts of magnetic materials added.

## 14.0 Scanning Electron Diffraction

Personnel: Professor S. C. Moss; J. F. Graczyk

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 75125

The construction of a scanning electron diffraction instrument has been completed. Essentially it consists of a JEM-6AS Electron microscope with X-Y scanning coils mounted below the high resolution diffraction chamber to allow a wide variety of programmable sweep modes. The diffracted electrons are then directed through the column of an electrostatic velocity filter whose grid (central electrode) is set, through direct coupling, at the accelerating potential of the microscope and they are detected with a p-n junction detector. The grid potential can be varied about this high voltage (HV) by an amount: $|HV + 6|$ to $|HV - 103|$ ev. w where HV is typically 50-80 KeV. The filter has a measured cut-off, or inherent energy window, of 1.3 ev. which we hope to improve to ~0.7 ev., and can be operated in either an integral or differential mode. In integral (D.C.) the filter passes all electrons with energy greater than HV - ev. where ev. is the bias voltage above. In differential (A.C.) it measures all electrons within the band HV - ev. ± $\phi$ where $\phi$ is the amplitude of an A.C. modulation impressed on the filter. Diffracted currents down to $10^{-15}$ amp. with a .1 sec. time constant can be measured and weaker intensities can be detected with a longer time constant.

The instrument will be used in two modes: (a) to measure the intensity distribution of purely elastically scattered electrons, (b) to measure the energy distribution of the inelastically scattered electrons. We are currently studying the variation with dilute alloying of the nominally 14.9 ev. plasma loss peak in Al to determine the variation in the plasma frequency, $\omega_p$, plasma dispersion $\omega$ versus k, and mean free path $\lambda$. The alloying element is Zn which has a wide range of solubility in Al. For the preliminary diffraction sutdy, we are going to determine the radial density functions of vapor deposited films of amorphous Si heat treated in various ways. We are also investigating the plasma loss peak in this amorphous semiconductor and will attempt to relate this to the electronic structure of the material.

## 15.0 Mossbauer Effect in Iron Alloys

Personnel: Professor R. Kaplow; W. K. Choo (in cooperation with Professor M. Cohen)

Sponsorship: Office of Naval Research, Nonr-1841(35), DSR 77618

The work on interstitial impurities in iron carbon and iron nitrogen alloys is continuing. In addition to conventionally prepared specimens, splat-cooled alloys, containing other impurities are being studied.

## 16.0 Structure of Liquids

Personnel: Professor B. L. Averbach, R. Kaplow; J. M. Franz and S. C. Lee

Sponsorship: National Science Foundation, GK-1947, DSR 70847

The detailed relationships between distribution functions and interaction potentials are being studied in selected pure and alloyed liquids, and descriptive models are being developed for the atomic arrangements and the dynamics. The Rahman method of using the interaction potentials is being used to study variations in potential shapes and asymmetries of two component systems. The study of supercooled and complex liquids is also being undertaken, using low angel diffraction, in order to study interaction pair potentials. Pair distributions are also being examined by neutron diffraction. Isotopic concentrations of the elements are being varied, and the radial distribution function for multi-element materials will be resolved for the individual pair distributions.

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J. E. Woodilla, "Composition Fluctuations in Gold-Nickel Alloys", Sc.D. Thesis, Department of Metallurgy, February 1967.

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K. H. Johnson, "The Energy Bands and Fermi Surfaces of IB-IIB Alloys", in Symposium on the Status of Energy Band Theories for Metals and Alloys, Proceedings of AIME Meeting in Los Angeles, (Gordon and Breach Science Publishers, Inc., New York), (in press).

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P. C. Clapp, S. C. Moss, "Correlation Functions of Disordered Binary

Alloys-II", Phys. Rev.

S. C. Moss and P. C. Clapp, "Correlation Functions of Disordered Binary Alloys-III", Phys. Rev.

S. L. Strong, and R. Kaplow, "Structure of Crystalline $B_2O_3$", Acta Cryst.

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## II. PHYSICAL METALLURGY - Phase Transformations, Metastable Phases, Diffusion, Structure-Property Relationships, Strengthening Mechanisms, Plastic Deformation

Personnel

(All personnel from Department of Metallurgy and Materials Science)

Professor M. Cohen, Ford Professor of Materials Science and Engineering

Professor H. H. Johnson, Visiting Professor

Professor J. F. Breedis, Assistant Professor

Dr. F. S. Gardner, Visiting Scientist

A. Sherman, Part-time Instructor

A. J. Gregor, Technical Instructor

G. T. Eldis, NASA Trainee

F. Fletcher, Research Assistant

D. S. Gelles, NSF Trainee

D. A. Karlyn, Research Assistant

M. K. Koul, Research Assistant

S. R. Pati, Research Assistant

H. J. Rack , Research Assistant

R. C. Ruhl, NSF Fellow

D. B. Snow, Research Assistant

I. Sprung, Research Assistant

R. Stevenson, Research Assistant

M. R. Vukcevich, Research Assistant

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E. D. Sudenfield, Technician

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Degrees Granted

D. A. Karlyn, Sc. D., June 1967

S. R. Pati, Sc. D., September 1967

R. C. Ruhl, Ph. D., September 1967

I. Sprung, M. S., June 1967

M. R. Vukcevich, Ph. D., September 1967

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United States Steel Corporation, DSR 70216
Vasco Metals Corporation, 21990
National Science Foundation Fellowship
NASA Traineeship
Wright Air Development Center, Contract AF 33(615)-3866, DSR 76337

Research Report

1.0 Strain-Enhanced Diffusion

Personnel: Professor M. Cohen; M. Vukcevich

Sponsorship: Atomic Energy Commission, AT(30-1)-2879, DSR 78954

It has been demonstrated that the strain-enhanced diffusion in iron and in gold depend on the nature of the diffusing specie being investigated, thus proving that the phenomenon cannot be due to mechanical mixing caused by the plastic flow. At the same time, the concommitant creep rates during the diffusion/deformation experiments depend on the normal, rather than the enhanced diffusion coefficients. In view of the fact that the creep rates are controlled by vacancy diffusion, it must be concluded that the strain-enhanced diffusivity cannot be accounted for by a supersaturation of vacancies.

Satisfactory agreement is obtained by adopting a moving dislocation-pipe model. One consequence of this treatment is that the diffusivity along moving dislocations depends on the dislocation velocity. These strain-enhanced diffusivity experiments now provide a means of determining the contribution of high-diffusivity paths to diffusion phenomena.

2.0 Isothermal Nucleation of Martensitic Transformations

Personnel: Professor M. Cohen; S. R. Pati

Sponsorship: Office of Naval Research, Nonr-1841(35), DSR 77618

The rates of isothermal nucleation of the martensitic transformation in iron-nickel-manganese alloys have been determined as a function of composition, austenitizing temperature, austenitic grain size, and reaction temperature. The nucleation rates show the expected C-curve behavior with respect to the reaction temperature. There is an apparent increase in nucleation rate with increasing austenitic grain size, but this results from the fact that the nucleation rates are normally determined at some fixed amount of transformation. It is now possible to deduce how the nucleation rates are affected by embryo consumption on the one hand and by autocatalytic factors on the other; based on this approach, the nucleation rates can be extrapolated back to zero transformation. The initial nucleation rates are found to be independent of the austenitic grain size as well as the austenitizing temperature. Accordingly, the preferred nucleation site cannot be confined to the austenitic grain boundaries.

The activation energies for nucleation vary with temperature in a manner predicted by the Kaufman-Cohen model, and the agreement becomes quantitative if an effective embryo radius of about 200 Å is assumed. The concentration of such initial embryos is of the order of $10^7$ $cm^{-3}$. Even though the embryos are large enough to be resolved by transmission electron microscopy, the probability of encountering them by this technique is extremely small.

## 3.0 Mössbauer Investigations of Iron-Base Interstitial Phases

Personnel: Professor M. Cohen, in collaboration with Professor R. Kaplow; W. K. Choo

Sponsorship: Office of Naval Research, Nonr-1841(35), DSR 77618

Mössbauer measurements are being used to shed light on the interaction between interstitial atoms and their neighboring host atoms in iron-base phases. The indications are that, in both austenite and martensite, the carbon is positively charged and strongly bonded to the adjacent iron atoms, whereas the nitrogen is negatively charged and weakly bonded to the adjacent iron atoms. On the other hand, carbon and nitrogen produce about the same tetragonal distortion in martensite and also cause the same degree of strengthening per interstitial atom. This interesting circumstance indicates that the interaction between dislocations and interstitial atoms in martensite is elastic in nature, rather than chemical or electronic.

## 4.0 Splat Quenching of Iron-Base Alloys

Personnel: Professor M. Cohen; R. Ruhl; F. Fletcher

Sponsorship: Office of Naval Research, Nonr-1841(35), DSR 77618; National Science Foundation Fellowship; United States Steel Corporation, Contract No. 5857, DSR 70216

In the splat quenching of iron-carbon-X alloys from the liquid state, an hexagonal close-packed phase is produced, containing 3.8 to 4.8 weight percent carbon. The lattice parameters increase linearly with carbon content, while the axial ratio remains essentially constant. This phase appears to be a solid solution of carbon in epsilon-iron, which is normally found only at high pressures. The carbon atoms exhibit an ordered arrangement corresponding to that of epsilon-iron carbide; the latter phase is based on a unit cell of composition $Fe_{24}C_{10}$, whereas the splat-quenched phase conforms to a unit cell of composition $Fe_{12}C_3$.

Silicon is found to stabilize the latter phase, and is being used to obtain this phase in bulk form so that its mechanical, electrical and magnetic properties can be measured.

Silicon also increases the amount of carbon that can be retained in austenite on splat quenching. The highest carbon content retained to date is 2.37 weight percent. This limit is imposed by the relative stability of the competing carbide phase. Similar trends are found in the nickel-carbon and cobalt-carbon systems: the less stable the respective carbide phase, the more carbon is retained in the supersaturated face-centered cubic solution by splat quenching.

## 5.0 Massive Transformations

Personnel: Professor M. Cohen, in collaboration with Professor J. W. Cahn; D. A. Karlyn

Sponsorship: Office of Naval Research, Nonr-1841(35), DSR 77618; Advanced Research Projects Agency, Contract No. SD-90, DSR 75125

A model for massive growth in the $\beta \rightarrow \alpha_m$ transformation in copper-zinc alloys has been extended from plane-front to spherical front growth. It is shown that in the one-phase region, diffusion-controlled growth of previously precipitated α-particles can accelerate to the point where the growth becomes interface-controlled instead of diffusion controlled. This constitutes the onset of the massive transformation, and the growth rate is then sufficiently rapid to preclude any significant concentration build-up ahead of the advancing interface. Under these conditions, the composition of the transformation product is the same as that of the parent phase.

In the two-phase region, the growth rate decelerates parabolically in the usual way, because of an increasing compositional build-up ahead of the interface, and the massive transformation cannot get started.

The kinetics explain why the massive transformation does not occur in copper-zinc alloys <u>above</u> a certain zinc content, and why the massive transformation cannot be inhibited on quenching from the all-β region in alloys <u>below</u> a certain zinc content.

## 6.0 Strain Hardening at Very High Strains

Personnel: Professor M. Cohen; H. J. Rack

Sponsorship: Vasco Metals Corporation, 21990

In wire-drawing studies, iron and iron-titanium alloys undergo a linear rate of strain hardening up to the highest strains investigated (99.9 percent reduction in area). Elongated cells or subgrains are produced by the deformation process, and the strengthening is inversely proportional to the cell size in the transverse direction. The cell size is controlled by the wire texture being generated and by simultaneous dynamic recovery. The cellular refinement continues up to the maximum wire-drawing strain, unlike the case of face-centered cubic metals, and seems to be a property of the body-centered cubic structure. Because the interstitial impurities are taken out of solution by the titanium, interstitial pinning of the cell walls cannot account for the progressive refinement of the cells.

Titanium contributes solid-solution strengthening, but does not affect the dependence of strain hardening on the transverse cell size. Moreover, the removal of strain hardening by subsequent annealing treatments is primarily governed by growth of the cells. In fact, this cell-size parameter seems to be the main independent variable in the strengthening process, when dealing with high degrees of plastic deformation, irrespective of the titanium content and recovery treatment.

Although the strain hardening is accompanied by a reduction in ductility on testing at room temperature, the low-temperature ductility is actually greater after the deformation process than before. This results from the cellular refinement which inhibits both mechanical twinning and cleavage fracture.

## 7.0 Strengthening of Steel by Thermomechanical Treatments

Personnel: Professor M. Cohen; G. T. Eldis

Sponsorship: Bethlehem Steel Corporation, DSR 79671

Iron-nickel-carbon martensites can be appreciably strengthened by thermomechanical treatments such as ausforming and strain tempering, even though carbide-forming elements are not present. The strengthening mechanisms are attributed to a high density of dislocations pinned down by carbon atoms which migrate into the dislocation stress fields. The carbon/dislocation interaction is so strong that the epsilon-carbide precipitation stage can be avoided during subsequent tempering; this permits the dislocations to remain locked at higher tempering temperatures than usual.

The effects of carbide-forming elements on these phenomena are now being investigated, using chromium and molybdenum as alloying elements. The base compositions are iron-nickel-carbon adjusted to lower the martensitic transformation temperature below the ambient. The martensite, thus formed are in the virgin condition, and the various stages of aging on heating below as well as above room temperature can be followed. Efforts are being made to detect the initial ordering of the carbon atoms in the stress fields of dislocations, prior to their migration towards the dislocation cores.

## 8.0 Development of Ultrahigh Strengths in Steel

Personnel: Professor M. Cohen; A. Sherman

Sponsorship: Bethlehem Steel Corporation, DSR 79671

The main purpose of this program is to raise the attainable strength level of martensitic steels by combining the available strengthening mechanisms, especially sequences of mechanical and thermal treatments. Very high densities of dislocations can be built up in martensites, whether tempered or untempered, by plastic deformation, and this type of processing will be extended to wire drawing. In this way, it should be possible to take advantage of cell-size refinement especially since carbon pinning should retard the dynamic recovery. A further alternative will be to carry out the plastic deformation at subzero temperatures where, again, dynamic recovery should be minimized. It is already known that when a small cell size is generated by appropriate deformation, the cell walls are surprisingly resistant to migration during subsequent recovery treatments.

9.0 Ferromagnetic Ordering in Alloys

Personnel: Dr. F. S. Gardner

Sponsorship: Office of Naval Research

The Bitter technique has been applied to several palladium-rich compositions in the Pd-Co system that are ferromagnetic up to and slightly above room temperature. The annealed sample of Pd-15 a/o Co evidences a complex macrostructure composed of small lath-shaped domains. The structure manifests a definite uniaxial symmetry in the unmagnetized condition, which is accentuated at the peaks of magnetization in fields of several hundred oersteds, in either of the two possible senses. It has not yet been feasible to distinguish unique regions differing in appearance, which might be nonmagnetically ordered regions.

While the observed uniaxial symmetry strongly suggests a noncubic crystal structure, the Pd-Co solid solution is reported to be always disordered and face-centered cubic. It is planned to continue the investigation along these lines, together with an assessment of chemical ordering.

10.0 Martensitic Transformations in Fe-Ru

Personnel: Professor J. F. Breedis; I. Sprung

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75128

The crystallography, morphology and defect structures of martensite have been investigated in iron-ruthenium alloys containing from 7.5 to

17.0 atomic percent ruthenium. Depending upon composition, two types of transformation products are observed: body-centered cubic martensite ($\alpha'$) similar to that found in stainless steel occurs in alloys containing up to 11.0 atomic percent ruthenium, while hexagonal close-packed martensite ($\epsilon'$) forms in more concentrated alloys. The orientation relationships between the parent austenite and the $\alpha'$ and $\epsilon'$ structures, determined through electron diffraction, are near the Kurdjumov-Sachs and the cobalt-transformation relationships, respectively. While many of the $\alpha'$ crystals are twin-related, the interface plane between such crystals is found to deviate from the expected twinning plane by nearly 17 degrees. This deviation can be explained by cooperative slip on closely spaced planes to produce a displaced interface plane. Observations of defect structures show that the stacking fault energy of austenite is around zero, while this energy is finite in $\epsilon'$ where unit dislocations were observed in addition to numerous partial dislocations. Consideration of the variations of the $M_s$-temperature and the extent of transformation with composition indicates that $\epsilon'$, which has a higher $M_s$-temperature, may assist in the nucleation of $\alpha'$, but otherwise hinders its growth.

## 11.0 Deformation of H. C. P. Alloys

Personnel: Professor J. F. Breedis; D. B. Snow

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75128

The deformation behavior of the hexagonal close-packed solid solution in the iron-ruthenium system is being studied as functions of composition, temperature and strain-rate. Specific topics under consideration include: (1) identification of operating slip and twinning systems, (2) character of dislocation arrangements and, (3) elucidation of mechanisms which control the deformation process. Techniques for thin-foil preparation have been developed through the use of a potentiostat to control polishing conditions. Progress is being made in evaluating the character of lattice defects through dark-field electron microscopy.

## 12.0 Fatigue of Titanium Alloys

Personnel: Professor J. F. Breedis; R. Stevenson

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75128

The objective of this investigation is to correlate the fatigue behavior of titanium and its alloys with defect substructures produced during cyclic stressing. The principal variables are composition, temperature, strain amplitude and grain size. The compositions under investigation include the hexagonal close-packed Ti - 4.5 Wt. % Al (disordered), Ti - 9 Wt. % Al (short-range order), and pure titanium, and body-centered cubic titanium-molybdenum alloys. While the fatigue behavior is presently being studied in polycrystals, single crystals will also be used in hope of more clearly resolving the dislocation-defect interactions which determine fatigue behavior. Transmission electron microscopy is being applied to evaluate the defect substructures resulting from deformation.

## 13.0 Strengthening of Titanium Alloys

Personnel: Professor J. F. Breedis; M. K. Koul

Sponsorship: Air Force Materials Laboratory, AF 33(615)-3866, DSR 76337

In conjunction with the study of fatigue behavior, the dependence of strength upon structures developed through plastic deformation and phase transformations is being studied in pure titanium, and in binary titanium alloys which contain aluminum, molybdenum or vanadium. Transmission electron microscopy is used to relate mechanical properties to structures developed through conventional tensile deformation, rolling, shock deformation at applied pressures of 75 and 200 kilobars, precipitation of omega-phase and martensitic transformation. Preliminary observations indicate that enhanced strengths without drastic loss of ductility can be attained through either shock deformation or controlled precipitation of the omega-phase.

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Satya R. Pati, "Nucleation of the Isothermal Martensitic Transformation in Iron-Nickel-Manganese Alloys," Sc.D. Thesis, Department of

Metallurgy and Materials Science, September 1967.

Robert C. Ruhl, "Splat Quenching of Iron-Base Alloys," Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1967.

Ivan Sprung, "Martensitic Transformation in Iron-Nickel-Manganese Alloys," M. S. Thesis, Department of Metallurgy and Materials Science, June 1967.

Milan R. Vukcevich, "Strain-Enhanced Diffusion," Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1967.

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## III. PHYSICAL METALLURGY - Thermodynamics of Metallic Systems; Properties of Solid Solutions; Deformation; Radiation Damage

### Personnel

Professor M. B. Bever, Professor, Metallurgy
Dr. A. K. Jena, DSR Staff, Metallurgy
R. O. Scattergood, Research Assistant, Metallurgy
L. I. Sudenfield, Project Technician, Metallurgy
Theresa R. Walsh, Secretary, Metallurgy

### Personnel who have left during the period

Professor G. E. A. Bartsch, Visiting Associate Professor, Metallurgy
Dr. A. Gangulee, DSR Staff, Metallurgy
A. M. Reti, Research Assistant, Metallurgy
Dr. J. Waldman, Research Assistant, Metallurgy

### Degrees Granted

A. Gangulee, Sc.D., Department of Metallurgy, February 1967
A. M. Reti, S.M., Department of Metallurgy, February 1967
J. Waldman, Sc.D., Department of Metallurgy, September 1967

### Sponsorship

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Office of Naval Research, Nonr 3963(19), DSR 74675
U. S. Atomic Energy Commission, AT(30-1)-1002, DSR 76831
National Aeronautics and Space Administration, Grant NsG-496, DSR 74569
Ford Foundation under the Massachusetts Institute of Technology - Technical University Berlin Faculty Exchange Program

### Research Report

This research was concerned with the thermodynamics of metallic systems, the properties of solid solutions, the deformation of metals and alloys and the effects of radiation on electronic materials. The experimental techniques used included liquid metal solution calorimetry, electrical measurements, X-ray and neutron diffraction and mechanical tests.

## 1.0 Thermodynamics of Metallic Systems

### 1.1 The Dilute Solutions of Gold and Antimony in Liquid Tin; Heat of Formation of $AuSb_2$

Personnel: Professor M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research, Nonr 3963(19), DSR 74675

The heat of formation of the compound $AuSb_2$ at $273^oK$ and the partial gram-atomic enthalpy of antimony in liquid tin at $623^oK$ have been measured. Values of the partial gram-atomic enthalpy of gold and the enthalpy interaction coefficients of gold and antimony in liquid tin at $623^oK$ have been calculated from the heat effects on solution of mixtures of gold and antimony in liquid tin. For the interpretation of the behavior of antimony and gold in dilute solution in tin, non-zero values were assigned to the energies of bonds between like solute atoms relative to the pure solute state.

### 1.2 The Metastability of Splat-Cooled Gold-Antimony Phases

Personnel: Professor M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research, Nonr 3963(19), DSR 74675

The metastable gold-antimony phases $\zeta$ (h.c.p.) containing 15.0 at. pct Sb and $\gamma$ (simple cubic) containing 76.6 pct Sb were prepared by splat cooling. Their heats of formation were measured by solution calorimetry and their free energies were estimated. An analysis of the free energies shows that the phases $\zeta$ and $\gamma$ are unstable at all temperatures. Melts having the composition of these phases must be undercooled by at least $150^o$ and $200^oK$, respectively, for $\zeta$ and $\gamma$ to form. Although the free energies indicate that the $\gamma$ phase is more unstable than the $\zeta$ phase, the calculated degrees of undercooling required and the calculated temperature of formation of the two phases show that the $\psi$ phase is less difficult to produce by splat cooling than the $\zeta$ phase, which is in agreement with experimental observations. This investigation has been conducted in collaboration with Professor N. J. Grant and Dr. B. C. Giessen.

## 1.3 Thermodynamics of Phases in the System Gold-Tin

Personnel: Professor M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research, Nonr 3963(19), DSR 74675

Several metastable phases can be prepared by splat cooling liquid gold-tin alloys. Knowledge of their thermodynamic properties will contribute to the understanding of the metastability of these phases and of the unusual behavior of liquid gold-tin alloys reported in the literature. Preliminary calorimetric and X-ray measurements on the metastable phases have been made. This investigation is being conducted in collaboration with Professor. N. J. Grant and Dr. B. C. Giessen.

## 2.0 Properties of Solid Solutions

## 2.1 Properties of the Solid Solutions of Lead Telluride and Lead Selenide

Personnel: Professor M. B. Bever; A. Gangulee

Sponsorship: Atomic Energy Commission, AT(30-1)-1002, DSR 76831

The structure of the solid solution alloys $PbTe_xSe_{1-x}$ $(0 \leq x \leq 1)$ was investigated by X-ray diffraction after different thermal treatments; microhardness measurements were also made. The lattice parameter of these solid solution alloys changed linearly with composition. The integrated intensity measurements gave no indication of an order-disorder transition in $PbTe_xSe_{1-x}$ at the compositions $x = 0.20$, $0.25$, $0.33$, $0.50$, $0.67$, $0.75$, and $0.80$. The microhardness of the alloys showed little solid solution hardening and did not change measureably with thermal treatment.

## 2.2 Long-Range Order in $Ag_3Mg$

Personnel: Professor S. C. Moss; A. Gangulee

Sponsorship: Atomic Energy Commission, AT(30-1)-1002, DSR 76831

The long-range order in the long-period superlattice of $Ag_3Mg$ has been investigated by powder X-ray diffraction as a function of quenching temperature below the critical ordering temperature of 665°K. The measurements indicate that the antiphase boundaries disorder slightly more with increasing temperature than the overall superlattice and that the average boundary spacing increases from about 1.95 to about 1.98 unit cells with increasing disorder below the critical point. These results suggest that it is the relative sharpness of the Fermi surface which is important in the stabilization of the long-period structure.

## 2.3 The Structure of the Alloys $Cu_x(NiZn)_{1-x}$

Personnel: Professor G. E. A. Bartsch

Sponsorship: Ford Foundation

The investigation of the alloys $Cu_x(NiZn)_{1-x}$ was completed. Neutron diffraction of polycrystalline samples showed superlattice lines, the positions of which agreed with those of a primitive cubic $L1_2$ structure. Samples of highly ordered, coarse grained $Cu_2NiZn$ were prepared by using the isotope $Ni^{60}$ in place of the naturally occurring Ni in order to distinguish on the basis of the diffracted intensities between two possible types of atomic arrangements in this ternary alloy: (a) an ordered structure of the type $(Cu_2Ni^{60})Zn$ with Zn at (0, 0, 0) and $(Cu, Ni^{60})$ at (½, ½, 0) and (b) an ordered structure of the type $(Cu_2Zn)Ni^{60}$ with $Ni^{60}$ at (0, 0, 0) and (Cu, Zn) at (½, ½, 0). The measured intensity ratios of superlattice to fundamental reflections were compared with the calculated ratios for cases (a) and (b). This comparison indicated that, in ordered $Cu_2NiZn$ alloys, the zinc atoms occupy the positions (0, 0, 0) as in case (a).

## 3.0 Deformation

## 3.1 Yield Phenomena in Silver-Cadmium Solid Solution Alloys

Personnel: Professor M. B. Bever; J. Waldman

Sponsorship: Atomic Energy Commission, AT(30-1)-1002, DSR 76831

In the investigation of the deformation behavior of silver-rich silver-cadmium solid solution alloys, specimens containing up to 38.3 at. pct cadmium were subjected to various cycles of tensile loading, unloading and aging. At room temperature, yield points were observed and became more pronounced with increasing cadmium concentration, aging time, and the stress under which the specimens were aged. At $78^{\circ}K$ and $195^{\circ}K$, yield points occurred during some of the cycles. Serrated stress-strain curves were observed at room temperature.

3.2 <u>Effect of Short-Range Order on the Deformation of Copper-Aluminum Alloys</u>

Personnel: Professor M. B. Bever; R. O. Scattergood

Sponsorship: Atomic Energy Commission, AT(30-1)-1002, DSR 76831

The investigation of the relation between short-range order and deformation behavior of the copper-rich terminal solid solution alloys in the system copper-aluminum was continued. Tensile tests and microhardness measurements were made on single crystals as a function of composition, orientation and heat treatment. X-ray diffraction measurements of the relative changes in short-range order as a function of heat treatment are in pr[illegible]or a given aluminum content and crystal orientation, increasing amounts of short-range order increase the yield drop but do not signficiantly affect other aspects of the deformation behavior, such as the flow stress and work hardening.

3.3 <u>The Annealing Behavior of Cold Worked AgMg</u>

Personnel: Professor M. B. Bever; A. K. Jena

Sponsorship: Atomic Energy Commission, AT(30-1)-1002, DSR 76831

An investigation of the annealing behavior of cold worked specimens of the intermetallic compound AgMg by resistometric and calorimetric measurements is in progress. Results obtained to date indicate the presence of annealing stages at about 115°C in the compound containing 50.1 at. pct Mg and about 0°C in the compound containing 44.2 at. pct Mg. The isothermal annealing behavior at several temperatures of the alloy containing 50.1 at. pct Mg has also been investigated.

## 4.0 Radiation Damage of Electronic Materials

Personnel: Professor M. B. Bever; A. Gangulee

Sponsorship: National Aeronautics and Space Administration, Grant NsG-496, DSR 74569

Specimens of polycrystalline $Bi_2Te_2Se$ were irradiated with 7.5 MeV protons to a maximum integrated dose of $2 \times 10^{16}$ protons/$cm^2$. They were examined by X-ray diffraction with crystal-monochromated cobalt $K\alpha$ radiation. The state of order in $Bi_2Te_2Se$ is described in terms of a modified long-range order parameter S, which depends on the positions of Te and Se atoms in the lattice. The long-range order was reduced progressively with increasing dose of irradiation. The rate of reduction of order was greater for a specimen having a higher degree of initial order.

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J. Waldman, "Properties and Deformation by Cold Work of Silver-Rich Silver-Cadmium Solid Solution Alloys," Sc.D. Thesis, Department of Metallurgy, September 1967.

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## IV. PHYSICAL METALLURGY - Phase Transitions in Solids, Coarsening, Radiation Damage, and Condensation in Nozzles

### Personnel

(All personnel from the Department of Metallurgy and Materials Science)

Professor J. W. Cahn, Professor
Professor K. C. Russell, Assistant Professor
J. Goldman, Part-time Instructor
J. Baker, NSF Trainee, and Part-time Instructor
S. Bhattacharyya, Research Assistant
C. Biswas, Research Assistant
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J. Johnson, Research Assistant
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J. Morral, Research Assistant
M. Richards, Research Assistant
J. Sandor, Research Assistant
J. Wells, Research Assistant
W. Carrasco, Technician
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### Personnel who have left during the period

D. A. Karlyn, Research Assistant (Now with Bethlehem Steel Corporation)
D. B. Dawson, Research Assistant (Now with General Electric Corporation)

### Degrees Granted

D. A. Karlyn, Sc.D., Metallurgy, June 1967
D. B. Dawson, S.M., Metallurgy, June 1967

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Office of Naval Research, Nonr-3963(07), DSR 79809
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## Research Report

### 1.0 Massive Transformation in Beta Brass

Personnel: Professors J. W. Cahn, M. Cohen; D. A. Karlyn

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75125

A capacitor-discharge pulse-heater has been built which permits heating rates of $10^{7}$ °C/sec. It is being used to study extremely fast solid state reactions in metallic systems.

The massive $\beta \rightarrow \alpha$ transformations in brass take about 10 milliseconds to complete at 500°C. The massive $\alpha$ phase starts at $\beta$-grain boundaries and grows into the $\beta$ grain with a measured growth rate of about 1 cm/sec. The transformation occurs only in the limited range of temperature and composition corresponding to the single-phase $\alpha$ region of the phase diagram. This simple experimental fact leads to some very important conclusions about the nature of the massive transformation.

### 2.0 Theory of Spinodal Decomposition

Personnel: Professor J. W. Cahn; J. E. Morral

Sponsorship: National Institutes of Health, Contract DE02384-02, DSR 70341

A theoretical basis for selecting ternary additions to raise or lower the reaction temperature for spinodal decomposition in binary alloys was established as part of a continuing study on multi-component systems. The study further predicted that ternary phases could be unstable to spinodal decomposition and ordering simultaneously, an untenable possibility in binary alloys. A simple construction based on binary interaction coefficients were also used to estimate the start temperatures for these reactions. This treatment differed from previous work chiefly by the inclusion of coherency strain energy which tends to stabilize phases. Future work will use the above concepts in attempts to control the age hardening behavior of gold-nickel base alloys.

### 3.0 Electron Irradiation

Personnel: Professor K. C. Russell; J. M. Wells

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75129

Work is proceeding on the electron irradiation of body-centered cubic metals at 4.2°K. This work is intended to identify the nature and magnitude of the damage and study the kinetics of annealing in these materials and their dilute interstitial alloys. We believe the annealing peaks will be very well defined. If so, we hope to determine the migration energy of the solvent interstitial atom as well as using the activation plots to identify the various stages and substages of annealing.

### 4.0 Nucleation in Nozzles

Personnel: Professors K. C. Russell, P. G. Hill (Mechanical Engineering); D. Dawson, R. Roberts

Sponsorship: Office of Naval Research, Contract No. Nonr-3963(07), DSR 79809

The digital computer has made the supersonic nozzle a powerful tool for the study of homogeneous condensation droplet growth. The nozzle does not suffer from the transient and contamination problems of the cloud chamber and the data are readily analyzed via computer. We have studied nucleation in vapors of water, carbon dioxide, ammonia, chloroform, benzene and Freon 11. The first two vapors follow the classical nucleation theory of Becker and Doering. The remainder are in accord with the $10^{17}$ times faster nucleation rates predicted by Lothe and Pound. We have also determined mass accommodation coefficients for condensation on small droplets of the various liquids.

Mr. Roberts will study droplet coarsening in nozzles through laser light scattering and has constructed the needed equipment. His technique is unique in using a long, very slightly divergent nozzle that will permit him to study droplet development from the moment of nucleation to long times.

## 5.0 Nucleation Involving Condensed Phases

Personnel: Professors J. W. Cahn, K. C. Russell; J. Baker, S. Bhattacharyya, C. Biswas, P. Boswell, R. Heady, J. Johnson, M. Richards, J. Sandor

Sponsorship: National Science Foundation, Contract No. GK 1304, DSR 70236

This is a broad theoretical and experimental investigation of the thermodynamics and kinetics of nucleation in condensed phases.

It has been postulated that splat-cooling extends the terminal solid solubility by quenching the melt below the extrapolated $\alpha/\alpha + L$ boundary to where the single-phase $\alpha$ is more stable than $L + \alpha$. Mr. Baker has shown this to be incorrent by obtaining extended solubility at the zinc end of the cadmium-zinc system which shows retrograde solubility. Mr. Baker has further shown that the usual assumption of interface equilibrium is not valid in this system and in fact one component is increasing its chemical potential upon solidification.

Mr. Heady has completed an analysis of the forces involved in liquid phase sintering of spheres, showing that the usual forces balance obtained intuitively is indeed very close to the exact solution. Mr. Heady is presently conducting the first test of homogeneous nucleation in condensed systems where all ancillary data on thermodynamics and surface tension are known.

We have cooperated with Dr. D. Hoffman of Ford Scientific Laboratory in entending the Gibbs-Wulff construction to determining the equilibrium form of a particle at a grain boundary of arbitrary orientation. Also with Dr. Hoffman we have reformulated the equations of capillarity in solids.

We have used the fluctuation theory of Von Smoluchowski and Tisza to analyze thermally activated nucleation and coarsening kinetics. This approach permits simple and unequivocal evaluation of frequency factors and incubation times for any nucleation case of interest. We have shown that in heterogeneous nucleation that incubation time may be as significant as steady state nucleation rate in determining which of several competing reactions will dominate. A theoretical formulation of coarsening still in progress indicates that the coarsening rates predicted by the Wagner-Lifshitz-Slyozov theory may be too low and their predicted particle size distributions may be too sharp.

We have analyzed the coherency strains for compositional inhomogeneities in elastically anisotropic crystals. These strains affect the free energy and lead to a new term in the diffusion equation for coherent processes. Anisotropy tends to stabilize either simple cubic or <111> arrays of particles, depending on the elastically soft directions.

## 6.0 Phase Separation and Crystallization in Glass

Personnel: Professor J. W. Cahn; J. H. Kitler

Sponsorship: Advanced Research Projects Agency, Contract No. SD-90, DSR 75125

The Kratky low-angle X-ray camera is presently being used to study phase separation in the $BaO-SiO_2$ glass system. This system which exhibits an asymmetric miscibility gap has been picked because of previous observations which have been made in the electron microscope both on slices from the bulk and samples which were vapor deposited. Low-angle X-ray studies on similar specimens would permit the first direct comparison between metallograph or "real space" data and its Fourier transform. This may help to clear some of the confusion which exists over morphology and decomposition mechanisms.

Theoretical work has been done on the X-ray scattering which is to be expected from particles with a diffuse interface. The integral of the intensity times the scattering angle raised to the fourth power is finite and propertional to the diffuseness of the interface. Expressions giving the form of the Debye correlation function have also been derived.

### Theses

D. A. Karlyn, "Massive Transformation in Copper-Zinc Alloys," Sc. D. Thesis, Department of Metallurgy, June 1967.

D. B. Dawson, "Condensation of Organic Vapors in a Supersonic Nozzle," S.M. Thesis, Department of Metallurgy, June 1967.

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J. W. Cahn, "The Significance of Average Mean Curvature and Its Determination by Quantitative Metallography", TMS-AIME 239, 610 (1967).

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K. C. Russell, "Comments on Phase Transitions during and after Film Deposition", J. Appl. Phys. 38, 4077 (1967).

K. C. Russell, "Linked Flux Analysis of Nucleation in Condensed Systems", Acta Met., in press.

## V. HIGH TEMPERATURE METALLURGY

### Personnel

(All personnel from Department of Metallurgy and Materials Science)

Professor N. J. Grant, Professor
Dr. B. C. Giessen, Research Associate
Dr. J. T. Blucher, Research Associate
Dr. H. Matyja, Research Associate
Dr. Rong Wang, Research Associate
P. Bridenbaugh, Research Assistant
H. Dalal, Research Assistant
R. Davison, Graduate Fellow
K. Erhardt, Research Assistant
G. Ewell, Research Assistant
F. Hunkeler, Research Assistant
C. Jansen, Research Assistant
R. Kane, Research Assistant
D. Kenagy, Research Assistant
W. Schilling, Research Assistant
W. F. Smith, Research Assistant
P. Knudsen, Special Student
W. Ioup, DSR Staff
U. Wolff, Engineering Assistant
T. Curran, Technician
M. Morris, Technician
Lydia E. White, Secretary

### Sponsorship

Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, F33615-67-C1441, DSR 70324
National Aeronautics and Space Administration, Washington, D. C., NsG-117-61, DSR 76243
Naval Air Systems Command, Department of the Navy, Washington, D. C., NOOO 19-67-C-0220, DSR 70297
Advanced Research Projects Agency, SD-90, DSR 75121

National Science Foundation, Washington, D. C., GK-1374, DSR 70290
U. S. Army Research Office, Durham, North Carolina, DA 31-124-ARO-D-328, DSR 74613
Office of Naval Research, Department of the Navy, Washington, D. C., Nonr 3963(18), DSR 74621

## Research Report

### 1.0 Dispersion Strengthening

Personnel: Professor N. J. Grant; F. Hunkeler, H. Dalal, W. Schilling, G. Ewell, D. Kenagy

Sponsorship: National Aeronautics and Space Administration, Office of Naval Research

Utilizing dilute Fe-Be alloy powders, Fe-BeO alloys ahve been prepared in extruded bar form. Extrusions were made both in the ferritic and in the austenitic regions. Hardness, tension properties, and stress rupture tests at 650°C. The materials will be studied to determine the role of stored energy of deformation as the probable mechanism of alloy strengthening (Mr. Hunkeler-NASA). The activity of Cr and $Cr_2O_3$ in oxidation resistant, oxide dispersion strengthened alloys and their effects on the stability of the refractory oxides (BeO and $ThO_2$) is being determined. At the same time, an effort is being made to produce materials suitable for service above 1100°C for long-time applications (Mr. Dalal-NASA). Cu-Al alloys have been comminuted to submicron flakes to provide powders which can be either surface oxidized or internally oxidized, resulting in a matrix of Cu which is solid solution strengthened by aluminum and dispersion strengthened by $Al_2O_3$ (Mr. Schilling-NASA). The deformation and fracture modes of oxide dispersion strengthened alloys are poorly known, expecially for alloys with oxide particles as fine as 50 to 200 Å and with particle spacings as fine as 0.2 micron. Both light and electron microscopy are being utilized to establish the behavior patterns. Where particles are finer than about 0.2 microns, transmission microscopy is being utilized (Mr. Ewell-NASA). Using five types of dispersoids at particle sizes from 0.01 to 25 micron, and at volume contents of 3 to 11 percent, copper-dispersion strengthened alloys are being studied to determine the mechanism of strengthening. (Mr. Kenagy-ONR)

## 2.0 Deformation and Fracture at Hot Working Temperatures

Personnel: Professor N. J. Grant; P. Bridenbaugh, R. Kane, W. Ioup

Sponsorship: Naval Air Systems Command

Mr. Bridenbaugh has studied both cast and wrought forms of pure Mo and the highly alloyed TZC composition to establish the mechanism of deformation and fracture. Being examined are the roles of strain rate, temperature, structure, and grain size on the resultant ductility at fracture. Efforts to improve hot plasticity by recrystallizing the structure are being made. Mr. Kane has performed similar studies with several grades of pure iron. He has achieved very large improvements in ductility at fracture by straining the cast materials at high strain rates to strains of 10 to 30%, followed by a holding time at temperature to allow grain refinement. A determination of the creep deformation process has been made. Mr. Ioup has established the very important role of grain size, chemical purity and particle cleanliness on the storage of energy of deformation, which leads either to grain growth (poor ductility) or grain refinement (improved ductility).

## 3.0 Equilibrium and Non-Equilibrium Alloy Phase Studies

Personnel: Professor N. J. Grant; Drs. R. Wang, B. C. Giessen, H. Matyja, J. T. Blucher; C. Jansen

Sponsorship: U. S. Army Research Office-Durham, Advanced Research Projects Agency, National Science Foundation, National Aeronautics and Space Administration

In this program, Dr. Wang is completing an investigation of pseudobinary $AB_3$ phase alloy systems containing gold and transition metal combinations; many structural analogies in the behavior of gold and the platinum group metals were observed. (ARO-Durham)

Dr. Giessen has participated in a comparative study of the binary alloy systems of gold with rare earths elements; he is continuing an investigation of the alloy chemistry of ordered transition metal alloy phases. (ARO-Durham; ARPA)

Dr. Matyja has completed an electron microscope study of the decomposition of metastable supersaturated Al-Si alloys; he has also participated in a determination of the dendrite size of splat cooled alloys as a function of the cooling rate. (NSF, NASA)

Mrs. Jansen is completing a study of the metastable solid solubilities of Cu, Ni, Co, and Fe in Al, and has initiated an electron microscope study of precipitation from some of these supersaturated solid solutions. Dr. Blucher continues in an effort to produce large quantities of rapidly quenched alloy material by extending the splat cooling process to larger quantities of powders; two atomization techniques have been developed each capable of producing useful powders over a range of quenching rates. (NASA)

Dr. Giessen has continued a study of metastable B-metal alloy systems; the scope is evident from the literature list. These studies have recently been extended to metastable transition metal alloy systems. (NSF, ARPA)

## 4.0 The Role of Strain Rate and Temperature in Low Strain Rate Fatigue

Personnel: Professor N. J. Grant; Dr. J. T. Blucher; P. Knudsen, K. Erhardt

Sponsorship: Aeronautical Systems Division

Dr. Blucher has extended the low cycle fatigue studies with high purity Al to include much wider range of strain rates (0.7 to 500%/minute) and total strains (.25 to 8%). These tests have permitted the fatigue life to be extended to over 100,000 cycles. The modes of deformation and fracture are being studied within this spectrum of test conditions. Dr. Blucher and Mr. Knudsen have studied the low cycle fatigue behavior of two SAP alloys ($Al-Al_2O_3$) from 20° to 427°C. The extreme stability of the SAP structure permits an evaluation of strain rate and temperature independent of continuously changing structure. Mr. Erhardt is performing similar studies with a commercial, age-hardening aluminum alloy, 2024-T4, this being a system in which structural changes occur readily above 150°C.

## 5.0 Aging in Al-Zn-Mg Alloys

Personnel: Professor N. J. Grant; W. F. Smith

Sponsorship: None

Mr. Smith is following precipitation phenomena in the Al-Zn-Mg systems, with particular emphasis on grain boundary depletion of precipitates. The roles of specific alloying elements (Cr, Ag, etc.) and of heat treatment on the depletion are being studied.

## 6.0 Development of Chromium Base Alloys

Personnel: Professor N. J. Grant; R. Davison

Sponsorship: Fairchild Fellowship

Mr. Davison is attempting to obtain a balance between strengthening (low and high temperature), the recrystallization temperature, the transition temperature for ductile to brittle fracture, and resistance to nitrogen pick-up at high temperatures. Stress has been placed on the important role of fine carbide dispersions and fine grain size on improving the performance of chromium as a base for useful alloys.

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B. C. Giessen, M. Morris, and N. J. Grant, "Metastable In-Bi Phases Produced by Rapid Quenching", Trans. Met. Soc. AIME, 239, p. 883 (1967).

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N. J. Grant, "Oxide Dispersion Strengthened Alloys", Second International Powder Metallurgy Conference, Stary Smokovec, Czechoslovakia, (1966).

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R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "Metastable Hexagonal Close-Packed Phases in Ni-rich Ni-Nb and Ni-Ta Alloys", J. Less Comm. Met. 13, p. 611 (1967).

B. C. Giessen, "Rapidly Quenched (Splat Cooled) Alloys" (Chapter). Strengthening Mechanisms Proc. of the 12th Sagamore Army Materials Research Conference, v. 12, Syracuse University Press (1966).

To be published

D. L. Ritter and N. J. Grant, "Modes of Deformation and Fracture of Low Cycle Fatigue of Aluminum as a Function of Temperature", Jour. Institute of Metals.

L. L. J. Chin and N. J. Grant, "Stored Energy in Dispersion Strengthened Alloys", AIME.

H. Matyja, B. C. Giessen, and N. J. Grant, "Dendrite Spacings in Rapdily Quenched Aluminum Alloys", J. Inst. of Metals.

M. Itagaki, B. C. Giessen, and N. J. Grant, "Supersaturation in Rapidly Quenched Al-rich Al-Si Alloys", submitted to ASM.

R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "New Microcrystalline Phases in Nb-Ni and Ta-Ni Alloys", Acta Met.

L. L. J. Chin and N. J. Grant, "Release of Stored Energy in Oxide Dispersion Strengthened Copper", Powder Metallurgy, London.

H. Matyja, B. C. Giessen, and N. J. Grant, "An Electron Microscope Study of the Precipitation of Silicon from Splat-Cooled Al-Si Alloys", submitted to AIME.

B. C. Giessen, U. Wolff, and N. J. Grant, "Metastable Simple Cubic Phases Based on Sb and Bi", AIME.

B. C. Giessen, U. Wolff and N. J. Grant, "The Metastable System Al-Ga and the Atomic Volume of Twelve-Fold Coordinated Gallium", J. Appl. Physics.

V. Sadagopan, B. C. Giessen, and N. J. Grant, "Crystal Chemistry of Gold-rich Alloy Phases with the Heavy Rare Earths", J. Less Comm. Met.

C. Gautier-Borromee, B. C. Giessen, and N. J. Grant, "Metastable Pb-Sb and Pb-Bi Alloy Phases", J. Chem. Phys.

## VI. PROCESS METALLURGY AND HIGH-TEMPERATURE CHEMISTRY

### Personnel

(All personnel from the Department of Metallurgy and Materials Science)

Professor J. Chipman, Professor Emeritus
Professor J. F. Elliott, Professor
Professor T. B. King, Professor
Professor D. J. Fray, Assistant Professor
S. Ban-ya, Research Associate
M. Onillon, Research Associate
W. B. Eisen, Research Fellow
C. W. Finn, Research Fellow
T. Kuwabara, Graduate Fellow
M. Maulvault, Research Assistant
H. Pielet, Research Fellow
B. Rosof, Research Fellow
G. K. Sigworth, Graduate Fellow
J. E. Sodi, Research Assistant
P. A. Tichauer, Research Assistant
J. C. Yarwood, Research Fellow
P. J. Yavorsky, Research Fellow
P. Bente, Undergraduate Student
Katherine Shepard, Undergraduate Student
J. Stack, Technician
Sylvia Harrington, Secretary
Barbara W. Wellnitz, Secretary

### Personnel who have left during the period

Olga Repetylo, DSR Staff
T. Adachi, Graduate Fellow
A. Coskun, Research Assistant
G. Delaval, Research Assistant
H. G. Hadrys, Research Fellow
J. E. Picard, Research Fellow
P. N. Dastur, Research Fellow

## Degrees Granted

A. Coskun, S.M., Metallurgy, September 1967

G. Delaval, S.M., Metallurgy, September 1967

H. G. Hadrys, Doctor's Degree, June 1967 (awarded by the Technical University of Berlin)

J. E. Picard, Sc.D., Metallurgy, June 1967

## Sponsorship

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Advanced Research Projects Agency, SD-90, DSR 78883
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American Iron and Steel Institute, Contract #146, DSR 70544
American Iron and Steel Institute, Contract #164, DSR 70542
National Bureau of Standards, CST-280, DSR 76360
National Science Foundation, GK-754, DSR 76235
United States Army, DAHC 04-67-C-0036, DSR 70368

## Research Report

### 1.0 Thermodynamics of Sulfides

Sponsorship: American Iron and Steel Institute and the National Science Foundation, GK-754, DSR 76235

Mr. Yavorsky is studying the thermodynamic properties of the (Fe, Mn)S system in the temperature range 700° - 1100°C in order to determine how the sulfide phase in equilibrium with a given Fe, Mn alloy changes its composition with temperature.

The electrochemical properties of $ThS_2$ and $BaS_2$ in the temperature range of 1000° to 1500°C are being studied by Mr. Sodi. He has measured their electrical conductivity when undoped and doped over the range of sulfur pressures, $-25 < \log P_{S_2} < 5$. He is also experimenting with these sulfides as possible sulfide-ion electrolytes for use in electrochemical cells at elevated temperatures.

Mr. Eisen has concluded his exploration of the existence of vapor species of the sulfides of the metals Cr, Mo, W, V, Ta and Nb. In this work he used a small mass spectrometer, and the experiments were restricted to temperatures at which the sulfides are solid (~ 1000° to 1300°C). Within the capability of the mass spectrometer used, no sulfide vapor species, other than those of pure sulfur, were found. The minimum detection pressure of the instrument was estimated to be approximately $10^{-8}$ atm. in the source Knudsen cell.

Mr. Eisen and Mr. Bente have been studying the temperature ranges over which CrS and $Mo_2S_3$ are stable. CrS decomposes to Cr and $Cr_7S_8$ at approximately 550°C. Mr. Bente is now completing a similar study on the decomposition of $Mo_2S_3$ to Mo and $MoS_2$.

## 2.0 Thermodynamics of Alloy Systems

Sponsorship: American Iron and Steel Institute and Army Research Office, DAHC 04-67-C-0036, DSR 70368

During the year Dr. Ban-ya and Professor Chipman completed an extended study of the thermodynamic properties of sulfur in liquid alloyed iron. The reaction $H_2(g) + \underline{S}$ (in alloy) = $H_2S(g)$ was used.

Dr. Ban-ya is now progressing on a study of the thermodynamic properties of carbon in alloyed austenite, using the reaction $CO_2(g) + \underline{C}$ (in alloy) = $2CO(g)$.

Dr. Onillon joined our group late in 1967. He is undertaking an experimental study of the behavior of carbon in alloyed austenite using an emf cell in which the electrolyte contains the ion $C^{2-}$. He is also planning to use the high-temperature solution calorimeter for the study of several liquid binary iron-alloy systems.

The use of a metallic absorber in the carrier-gas method for determining the vapor pressure of a component of an alloy has proved to be satisfactory. Using the modified method, Mr. Coskun completed a study of the activity of Al in liquid Al-Fe alloys at 1310°C.

In his year at M.I.T., Mr. Hadrys completed his analysis of the thermodynamic properties of chromium, phosphorus and carbon in the following systems: Fe-Cr, Fe-P, Fe-Cr-C, Fe-P-C, Fe-Cr-P, Fe-Cr-P-C(sat). The experimental work was done the previous two years at the Technical University of Berlin, under the supervision of Professor M. G. Frohberg.

3.0 Nucleation of Inclusions in Steel

Sponsorship: American Iron and Steel Institute

In a study which is supervised jointly by Professor M. C. Flemings and Professor Elliott, Mr. Yarwood is investigating the influence of the solidification process on the manner in which the non-metallic phases in iron-sulfur-oxygen alloys form and grow. A levitated pellet of the alloy is processed through a heating and cooling cycle. It is then quenched after a selected fraction of solidification has taken place.

Mr. Kuwabara, whose two-year program of study here is supported by the Fuji Steel Company of Japan, is undertaking a study of the effect of delayed solidification on the way that silicates grow in Fe-Si-O alloys.

4.0 Problems in Heat and Mass Transfer

Sponsorship: American Iron and Steel Institute, National Science Foundation, GK-754, DSR 76235

Mr. Sigworth is studying the factors that determine the rate at which particles of solid iron, and Fe-Al and Fe-Si alloys dissolve in liquid iron.

The effects which may cause circulation of the liquid during solidification of an ingot are under investigation by Mr. Pielet. He is modeling his systems by computer and is using an interrupted-quench technique in the laboratory.

The study of the temperature distribution in an arc furnace electrode, which was begun by Mr. Delaval, has been continued by Mr. Maulvault. Mr. Maulvault is also applying the same mathematical method to a study of the temperatures in the electroslag remelting system. He is constructing a small experimental unit to test the results of the analysis.

5.0 Structure of Liquid Oxides

Sponsorship: American Iron and Steel Institute

Dr. A. Boyer's work on the structure-sensitive properties of the phosphate melts is now being followed-up by an attack on the influence of additions of silica on the structure of phosphate melts. The study is being carried out by Mr. Finn, under the supervision of Professor Fray. The phosphate glass is dissolved in water and the species are analysed by paper chromatography. Hopefully, the study will provide some insight into the structure of liquid silicates containing metal oxides.

6.0 Kinetics of CO Evolution

Sponsorship: American Iron and Steel Institute

P. N. Dastur has completed his work on the evolution and adsorption of carbon monoxide by liquid iron. The desorption reaction is, at low carbon contents, controlled by the rate of the surface reaction which is very much affected by the adsorption of oxygen on the iron surface. The rate can be speeded up by the presence of carbon monoxide in the atmosphere or by deoxidation of the iron. The surface effect seems to be specific to oxygen since sulfur does not have a similar effect.

7.0 Low-Temperature Oxidation of Iron

Sponsorship: American Iron and Steel Institute

J. E. Picard completed his work on low temperature oxidation of iron, showing that, if the temperature was below about 500°C, oxidation of iron would proceed in a mixture of hydrogen and oxygen for which the equilibrium oxygen potential was less than that for the formation of iron oxide. If the gas was catalysed so that $H_2O$ was formed, oxidation did not take place. These observations are to be explained by competition between the catalysis by the iron of the reaction $H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$ and the formation of oxide on the iron surface.

8.0 Electroslag Melting

Sponsorship: American and Steel Institute

Mr. Tichauer has started work on the kinetics of electrode reactions as they pertain to the electroslag remelting process. In particular, he will study the elimination of sulfur from a liquid iron electrode and its removal from the electrolyte at an inert anode.

9.0 Irreversible Thermodynamics

Sponsorship: American Iron and Steel Institute

Mr. Rosof is nearing completion of a study of coupled reactions which has led to a reformulation of irreversible thermodynamics that is more general than previous treatments.

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A. Coskun, "Activity of Aluminum in Iron Alloys at 1315°C," S.M. Thesis, Department of Metallurgy, September 1967.

G. Delaval, "The Temperature Distribution in an Arc-Furnace Electrode," S.M. Thesis, Department of Metallurgy, September 1967.

H. G. Hadrys, "Thermodynamics of Multicomponent Metallic Solutions," Doctor's Thesis, awarded by the Technical University of Berlin, West Germany, June 1967.

J. E. Picard, "Oxidation of Pure Iron at Low Temperatures," Sc.D. Thesis, Department of Metallurgy, June 1967.

Publications

A.J. G. Boyer, D. J. Fray and T. R. Meadowcroft: "The Surface Tensions and Molar Volumes of the Binary Phosphates of Sodium, Lithium, Calcium and Zinc," J. Phys. Chem., 1967, vol. 71, p. 1442.

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J. Chipman: "Thermodynamics of Binary Fe-C Austenite and Cementite," Trans., TMS-AIME, 1967, vol. 239, pp. 2-7.

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H. R. Larson and J. F. Elliott: "The Standard Free Energy of Formation

of Certain Sulfides of Some Transition Elements and Zinc," Trans., TMS-AIME, 1967, vol. 239, pp. 1713-20.

C. H. P. Lupis and J. F. Elliott: "Oxygen-Alloying Element Interactions in Liquid Alloys," Trans., TMS-AIME, 1968 (in press).

R. Orr and J. Chipman: "Thermodynamic Functions of Iron," Trans., TMS-AIME, 1967, vol. 239, p. 630.

F. E. Woolley and J. F. Elliott: "Heats of Solution of Aluminum, Copper and Silicon in Liquid Iron," Trans., TMS-AIME, 1967, vol. 239, pp. 1872-83.

## VII. SURFACE CHEMISTRY

### Personnel

Professor P. L. De Bruyn, Professor, Metallurgy and Materials Science
E. Fouquet, Graduate Student, Metallurgy and Materials Science
P. R. Irissou, Research Assistant, Metallurgy and Materials Science
B. M. McLaughlin, NSF Trainee
J. W. Morris, NSF Trainee
Patricia E. Gavagan, Secreatry, Metallurgy and Materials Science

### Degrees Granted

P. R. Irissou, S.M., Metallurgy, February 1967
Y. G. Berube, Sc.D., Metallurgy, February 1967

### Sponsorship

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U. S. Army Research Office-Durham, DA-31-124-ARO-D-187, DSR 75039

U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, DA-AMC-18-035-76(A), DSR 75276

### Research Report

#### 1.0 Influence of the Structure and Composition of Clean Solid Surfaces on the Nature and Behavior of Solid-Fluid Interfaces

Personnel: Professor P. L. De Bruyn; E. Fouquet

Sponsorship: U. S. Army Research Office-Durham, DA-31-124-ARO-D-187, DSR 75039

The adsorption of the potential-determining ions, hydrogen and hydroxyl, at the nickel hydroxide-solution interface and at the nickel oxide-solution interface was studied by potentiometric titration and by pH drift. experiments. Sodium chloride at several ionic strengths was used as a supporting electrolyte at 25°C.

The study of the hydroxide system showed the interaction of several additional phenomena, one of them leading to a morphological change of the precipitate. When allowance was made for these phenomena a pzc was detected between pH 9 and pH 9.4. The important effect of ageing and conditioning was also investigated. Under some circumstances the detection of apoint of zero charge near pH 7.4 led to the reconsideration of the assumptions made in applying the potentiometric titration technique.

The similarity shown by some experimental results obtained in working with the hydroxide and with the oxide systems focussed attention on a possible surface rehydration of the oxide when in contact with an aqueous solution.

The influence of Fe(III) hydroxo-complexes in small concentration was investigated on the rutile system. Adsorption isotherms and surface capacitance curves are shown to be altered by the presence of hydroxo-complexes and a shift of the pzc to more acid values was observed. The effect was more important at high ionic strengths of the supporting electrolyte than at low ionic strengths.

## 2.0 Spreading of Liquids on High Surface Energy Solids Under Controlled Interfacial Conditions

Personnel: Professor P. L. de Bruyn; B. M. McLaughlin, J. W. Morris

Sponsorship: U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, DA-AMC-18-035-76(A), DSR 75276

As a continuation of the study of liquid spreading on high surface energy solids, a series of experiments with low surface energy solids was initiated. The types of liquids used were alkylbenzenes, chloroethanes and chloroethylenes. Other than Teflon, only hexafluoropropylene, oxtadecylamine adsorbates and the paraffins and waxes are known to exhibit measurable contact angles with these liquids. However, the possibility did exist that additional materials would exhibit a finite advancing angle with the liquids specified, even though the so-called equilibrium angle appears to be zero. Preliminary experiments with polyethylene, polypropylene and vikem vinyl, however, precluded this possibility.

Contact angles were measured by the half-submerged tilting plate method. The observations showed that (a) the apparent advancing and receding angles ($\theta_A$ and $\theta_R$) are virtually independent of speed in the 0.8 cm/min to 4 cm/min range, (b) any angle between $\theta_A$ and $\theta_R$ can be obtained by simply stopping the rod motion at the appropriate point; such angles are stable, and (c) $\theta_A$ and $\theta_R$ are functions of surface roughness.

## Theses

Y. G. Berube, "Adsorption of Inorganic Ions at the Titanium Oxide-Solution Interface", Sc.D. Thesis, Department of Metallurgy, February 1967.

P. R. Irissou, "A Study of the Preparation of Thin ZnS Films", S. M. Thesis, Department of Metallurgy, February 1967.

## Publications

Y. G. Berube, G. Y. Onoda, Jr. and P. L. deBruyn, "Proton Adsorption at the Ferric Oxide/Aqueous Solution Interface. II. Analysis of Kinetic Data", Surface Science 8, 448 (1967).

Y. G. Berube and P. L. de Bruyn, "Adsorption at the Rutile-Solution Interface: I. Thermodynamic and Experimental Study", accepted for publication in Journal of Colloid Science.

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## VIII. CERAMICS

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(All personnel from Department of Metallurgy and Materials Science.)

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Antoinette Centorino, Secretary
Susan Mogab, Secretary

## Degrees Granted

R. L. Anderson, Sc.D., September 1967
T. K. Gupta, Sc.D., February 1967
R. E. Mistler, Sc.D., June 1967
C. J. Mogab, Sc.D., February 1967
R. R. Shaw, Sc.D., September

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## Research Report

The current research program in ceramics can be broadly described as including: (1) research on kinetics of phase changes, diffusion, and the development of microstructure in ceramics, (2) relationship of properties to composition, crystal structure, and microstructure, and (3) research on the structure and properties of noncrystalline solids. Each of these areas of research is described in detail in the report.

## 1.0 Kinetics of Phase Changes, Diffusion, and Microstructure Development

Personnel: Professors W. D. Kingery, R. L. Coble, C. J. Mogab, D. R. Uhlmann, and B. J. Wuensch; R. L. Anderson, T. J. Brown, K. S. Kim, R. E. Mistler, J. C. Ohep, S. Prochazka, J. Sauvage, R. J. Tiernan, and P. J. Vergano

### 1.1 Grain-Boundary Diffusion Studies

Personnel: Professor B. J. Wuensch; R. J. Tiernan

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Polycrystalline bodies are usually involved in most practical situations in which diffusion may be a rate-controlling process. In such materials preferential diffusion along grain boundaries may greatly modify rates predicted on the basis of single-crystal diffusion data. Direct evidence for grain-boundary diffusion has been obtained for only a few ionic materials and oxides. The role of grain-boundary chemistry and grain orientation in the effect is not clear.

Diffusion rate for Tl (a highly polarizable ion for which transport should be greatly influenced by the presence of grain boundaries) are presently being determined in KCl. Two varieties of diffusion specimens are employed. By equilibrating the surface of a KCl specimen with a vapor of TlCl, the surface may be maintained at concentration during the course of the diffusion anneal. Alternatively, Tl solute has been supplied from an initial thin film of TlCl plated on the surface of the specimen. Concentration distributions are determined with the aid of an electron microbeam probe.

Diffusion coefficients for Tl in single-crystal KCl have been determined over a temperature range of $396^{o}$-$688^{o}C$. The results may be represented by

$$D = 9.18\ 10^{-3} \exp\ (-1.45\ eV/kT$$

and provide a basis with which subsequent measurements of grain-boundary diffusion will be compared. Diffusion rates are presently being measured in bicrystals of controlled orientation which were fabricated with the hot wire technique. Pressure-sintering and pulling of bicrystal seeds from a melt are also being explored as alternative techniques for bicrystal preparation.

## 1.2 Transport in Crystals Subjected to Stress

Personnel: Professor B. J. Wuensch; K. S. Kim

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773,
DSR 70112

The stress imposed on ceramics during processing or in their applications would conceivably alter transport rates in a number of ways. Pressure could modify the pre-exponential frequency factor, the volume of the activated complex, or both. Dislocations, introduced as a result of plastic deformation, may act as paths of enhanced transport, and the motion and intersection of dislocations may generate increased concentrations of point defects. Experiments performed with metals indicate that, at low temperatures, diffusion rates are independent of strain, but may be enhanced by several orders of magnitude by high strain rates. Data are lacking for ionic materials.

A study of transport in alkali halides during deformation has been initiated. The normal transport mechanism in these materials is fairly well understood, and further, diffusion rates and electrical conductivity may both be used to interpret changes in defect concentrations. Initial experiments will be concerned with measurement of conductivity as a function of strain, and as a function of strain rate, during deformation of a single crystal.

## 1.3 Crystallization and Melting Kinetics in Glass-Forming Systems

Personnel: Professor D. R. Uhlmann; P. J. Vergano

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773,
DSR 70112
National Science Foundation Fellowship

In glass-forming systems, measurements of crystallization and melting kinetics can be carried out over a wide range of temperature. At the present time such measurements are being carried out on $SiO_2$ and

$GeO_2$; and it is anticipated that the resulting data will be useful in elucidating the essential features of the crystal growth process.

In the case of germanium dioxide, measurements of crystal growth are being carried out in the temperature range between 700 and 1100°C (the melting point is 1115°C). Heterogeneous nucleation on the external surfaces has been observed to occur readily on reheating samples into this temperature range from the glassy state. Internal nucleation of crystals has not been observed. In all cases, even at magnifications of 600x, the crystal-glass interface morphology is non faceted.

Growth rates are determined from the variation with time of the thickness of the crystalline layer which proceeds inward from the surfaces. The growth rate has been found to depend upon the atmosphere in which the crystallization is carried out, as well as upon the original melting conditions. It has been found possible to produce $GeO_2$ glasses differing in water content and state of reduction by varying the atmosphere and temperature of melting.

The effect of residual water and state of reduction on the viscosity as well as the growth rate are being determined. The growth rate and viscosity data, obtained under similar conditions on similar samples, will be combined to obtain information on the nature of crystal growth from the melt.

## 1.4 Crystallization and Melting Kinetics at High Pressure

Personnel: Professor D. R. Uhlmann; T. J. Brown

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The effect of high pressure on the kinetics of crystallization and melting are being investigated both theoretically and experimentally. A previous analysis of the effect of pressure on the kinetics of nucleation and crystal growth has been extended to include its effect on incubation time and overall crystallization kinetics. The first materials being investigated experimentally are $SiO_2$, $B_2O_3$, and $NaAlSi_3O_8$ (albite).

## 1.5 Densification and Grain Growth in Powder Compacts

Personnel: Professor R. L. Coble; S. Prochazka, R. Mistler, and J. C. Ohep

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Densification in the intermediate stage of the sintering of zinc oxide, and pore growth and de-densification after prolonged sintering, have all been found to be quantitatively consistent with models in which the kinetics are assumed to be governed by transport in the lattice. The processes are quantitatively consistent with zinc ion self-diffusivity.

Investigations of the grain enlargement in two-phase systems has been carried out for various compositions between aluminum oxide and magnesium aluminate spinel. It is found that there is a significant inhibition to growth by the increased volume fraction of the second phase and that the growth rate varies with time to the one-third power. Continuation on the problems associated with intermediate stage sintering and grain growth are related to: measurements of the change in pore size distribution and grain size with time. Measurements now under way in this area are to delineate the importance of surface diffusion to pore growth during the process.

Grain boundary migration velocities of secondary grains in high-purity silver, sodium chloride, and aluminum oxide show significant differences in characteristics. The grain boundary widths calculated from the data are much larger for the ionic compounds than for the metal. This larger width is attributed to an intrinsic difference in the region of disorder in ionic compounds consistent with the space charge models for differences in numbers of defects at the grain boundaries. Further work is needed to clarify impurity effects on the space charge effects and on intrinsic inhibition to boundary migration.

## 1.6 Oxygen Diffusion in $Al_2O_3$

Personnel: Professor R. L. Coble; R. L. Anderson

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The diffusivity of oxygen ions in aluminum oxide has been remeasured using an activation analysis of $O^{18}$ and a sectioning technique. Oishi and Kingery's results were generally confirmed. The higher precision with lower scatter in the present measurements is attributed to better sample characterization; the diffusivity was found to be dependent upon dislocation density within the crystals and independent of impurity contents present (in three different sets of samples). Continuation in this area is being made into polycrystalline samples and doping effects.

1.7 Kinetics of Processes Characterized by a Distribution of Activation Energies

Personnel: Professors W. D. Kingery and C. J. Mogab; J. Sauvage

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The phenomenological theory of processes distributed in activation energy is receiving further attention. To obtain complete information, it is important to know the shape, width, and functional form of the distribution. In the present study, the type of information is rough for very simple multiactivated processes; time, temperature dependence are studied; notions of annealing function and order are reviewed; the question of the number of parameters needed to describe the internal state and problem of linearity are evoked. Thermodynamics and kinetics of the phenomena may then be described. Finally, an attempt is made to interpret distributions of activation energies in terms of molecular models.

1.8 Pore-Grain Boundary Interactions

Personnel: Professor W. D. Kingery; G. A. Kemp

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Studies are just getting under way to determine further details of the interaction between pores and grain boundaries during heat treatment using fine particle-size monodisperse starting materials.

2.0 Relationship of Properties to Composition, Crystal Structure, and Microstructures

Personnel: Professors W. D. Kingery, R. L. Coble, and B. J. Wuensch; H. K. Bowen, S. A. Cho, J. A. Conwicke, P. N. Dangel, T. R. Guillermo, I. Kohatsu, A. Mocellin, J. J. Rasmussen

## 2.1 Crystal Structure Studies

Personnel: Professor B. J. Wuensch; S. A. Cho, P. N. Dangel, T. R. Guillermo, I. Kohatsu

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

### 2.1.1 Crystal Chemistry of Glass-Forming Sulfides

Personnel: Professor B. J. Wuensch; T. R. Guillermo

The phases $Sb_2S_3$ (which has a chain structure) and $As_2S_3$ (which has a layer structure) are well known constituents of sulfide glasses. An intermediate crystalline phase $AsSbS_3$ was recently discovered which bears no apparent relationship to the structures of either end-member in the system. A structure determination of crystals synthesized from $As_3SbS_6$ glasses under 1000 bars pressure is in progress. The relative arrangement of Sb and As in the phase should provide insight into the structure of the glasses formed in this system.

### 2.1.2 Rules for Formation of Tetrahedral Phases

Personnel: Professor B. J. Wuensch; P. N. Dangel

It has been possible to understand, in terms of valence electron concentration, the existence of over 200 phases in which the bonding occurs through $sp^3$ hybridization. These materials constitute many of the important semiconductor materials. A few exceptions to these rules exist, and it has been proposed that either the compositions assigned to them, the crystal structures reported for them, or both, are incorrect. One example is a phase assigned composition $Cu_3(As,Sn,V)S_4$, which occurs as the mineral colusite, and which may be obtained by pyrosynthesis. The phase had been reported to have the sphalerite structure. It has been found that supposed single crystals consist of an intergrowth of Sn-rich and Sn-poor phases. The true composition of these phases is being determined by microprobe analysis. It has also been found that the space group reported for the structure is not correct, and that the structure is actually a superstructure based upon the sphalerite arrangement.

### 2.1.3 Superstructure Based Upon the Rock Salt Arrangement

Personnel: Professor B. J. Wuensch; S. A. Cho, I. Kohatsu

Certain Pb-containing sulfides form complex superstructures based upon a rock salt-like arrangement of atoms, while other phases of similar composition do not. Determination of a number of these superstructures has been undertaken in an attempt to determine the conditions under which such phases may form and to understand why only a few of the many compositions possible are actually stable. A structure determination of $PbAgAsS_3$ has been completed. The structure superficially resembles the NaCl arrangement with an ordered arrangement of metal atoms. As, however, forms $p^3$ bonds with only three neighbors, and Ag is bonded to but four neighboring S. This results in a severe distortion of the S array, and these atoms are displaced by as much as 1.1Å from their ideal positions. The structure obtained differs from that reported for its Sb analogue $PbAgSbS_3$. The structure of the latter phase is therefore being redetermined and is nearly completion.

The pseudobinary system PbS-$As_2S_3$ displays at least 12 intermediate phases. The Pb rich compounds apparently have structures closely related to the rock salt arrangement. The structure of $Pb_{13}As_7S_{23}$ has been found to be a superstructure based upon two rock salt-like slabs rotated 120° about [111] with respect to one another. Determination of this superstructure is continuing.

### 2.1.4 Vacancy Ordering and Ferrimagnetism in the System Fe-S

Personnel: Professor B. J. Wuensch

The system Fe-S exhibits complex magnetic behavior which is still incompletely understood. Stoichiometric FeS is antiferromagnetic Departures from stoichiometry arise from Fe vacancies in a NiAs like structure. Near composition $Fe_7S_8$ the vacancies assume an ordered arrangement and the resulting superstructure exhibits ferrimagnetic behavior. A detailed structure determination is in progress.

### 2.1.5 Long-period Layer Silicates

Personnel: Professor B. J. Wuensch

Many traditional ceramic materials are layer silicates. The crystal chemistry of the Mn layer silicates is of interest because of the large dimensional misfit between Mn octahedra and the $Si_2O_5$ sheet commonly present in layer silicates. This may favor formation of silica layers with new configurations. In a preliminary study of some poorly defined members of this group it has been found that $Mn_8SiAsO_9(OH)_7$ has a lattice translation in excess of 200 Å, making it one of the largest periods known for an inorganic material. Despite the large magnitude of this translation, the structure is neither a superstructure nor a stacking polytype. This structure was further shown to be related to that of $Mn_{20}Si_3O_{26}(OH)_6$ and to $Mn_{13}Al_2As^{3+}As^{5+}{}_2O_{12}(OH)_{21}$. All phases have two lattice constants in common; and were shown to have structures which are nearly indistinguishable upon projection along the long cell edge. The structures probably consist of thick layers of which only portions are common to the three structures. The nature of an interaction which may be repeated over several hundred angstrom presents an interesting porblem in crystal chemistry, and further study of these phases is contemplated.

### 2.1.6 Non-stoichiometric Spinels

Personnel: Professor B. J. Wuensch; H. T. Anderson

Many ceramic systems possess an intermediate phase $XZ_2O_4$ which has the spinel structure. The stability field of this phase frequently extends over wide ranges of stoichiometry towards $Z_2O_3$. Spinel phases of various composition are being synthesized. Density measurements, combined with precision lattice constant determinations, will be used to determine the mechanism of solid solution. Additional work may explore the degree of disorder among the cation sites.

### 2.1.7 Structural Study of the Phase Transformation in CuAgS

Personnel: Professor B. J. Wuensch; T. R. Guillermo

The phase $Cu_2S$ exhibits an unusual unquenchable phase transformation in the neighborhood of 100°C. The transformation involves an unusual amount of energy, and both Cu self-diffusion rates and conductivity increase by several orders of magnitude. A structure determination of the high-temperature modification has shown that the Cu atoms are disordered, and migrate between 2-, 3-, and 4-coordination sites in a hexagonal close-packed S array. The relation to the low temperature form is unknown. This phase is extremely complex and contains 288 atoms per cell.

A similar phase transformation apparently exists in CuAgS. The room temperature structure is relatively simple. The structure of the high-temperature modification is unknown. High-temperature X-ray diffraction is being employed to determine the structure of both phases at several temperatures spanning the phase transformation. The resulting structural data will be used to relate changes in bond lengths to thermal expansion data, study atomic vibrations near the transformation point, and to determine variations of site occupancies with temperature in the disordered phase.

## 2.2 Preparation and Properties of High-Purity and Doped Single Crystal $Al_2O_3$

Personnel: Professor W. D. Kingery; J. J. Rasmussen

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The solid solution behavior of impurities in high-purity single crystal $Al_2O_3$ is being studied by examining density changes resulting from proposed solubility mechanisms compared with the measured changes. The densities of Czochralski grown white sapphire, titania-doped sapphire, and ruby from the Linde Division of Union Carbide Corp. were measured using a hydrostatic weighing technique. The standard deviations were better than $\pm 2.0 \times 10^{-4}$ g/cm$^3$. The X-ray densities agreed well with the measured densities for the solubility mechanisms selected. The results indicate that titania goes into solution in the $Al_2O_3$ lattice by a substitutional mechanism. The as-grown purple sapphire has a ratio of one $Ti^{4+}$ for each two $Ti^{3+}$. A clear sample which had been annealed in a gas-fired furnace indicated that some of the $Ti^{3+}$ ions had been oxidized to $Ti^{4+}$. As expected, the results indicated that chromium ions substitute directly for aluminum ions in ruby.

An electron beam technique has been used to zone-refine $Al_2O_3$ rods. Examination of the impurities left behind in sections of a rod through which the molten zone had been passed 0, 2, 4, and 8 times indicated that C, Mg, and U were the only impurities whose concentration was reduced by the zone-refining. The other impurities merely underwent zone leveling. It is desired to dope $Al_2O_3$ crystals with the zone melting technique. In a stationary molten zone there is little mixing of the dopant and the $Al_2O_3$. Rotating the molten zone causes a distribution to occur, but much of the dopant is lost through vaporization.

## 2.3 Thermophysical Properties of Nonstoichiometric Materials in a Thermal Gradient

Personnel: Professor W.D. Kingery; H. K. Bowen

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Thermal gradients are present during most high temperature applications of ceramic materials. In materials with a homogeneity region (e.g., $FeO_{1-x}$, $UO_{2-x}$), the composition as well as most physical proper ties are a function of temperature and therefore vary along the thermal gradient.

A material is to be selected which has a substantial homogeneity region and also one for which the thermodynamic properties are well known. Thus an attempt will be made to predict the thermophysical properties across the gradient as well as directly measuring them.

## 2.4 Properties of High Purity and Doped Polycrystalline $Al_2O_3$

Personnel: Professor W. D. Kingery; A. Mocellin

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

A study has been initiated on the influence of minor amounts of dopants in high-purity polycrystalline aluminum oxide. The purpose is to obtain information about the nature of solid solutions in $Al_2O_3$ and diffusional creep characteristics as affected by the defect structure of the material.

It does not seem possible to obtain a base $Al_2O_3$ powder with better than 20 to 30 ppm residual impurities. Doped powders are to be vacuum hot-pressed to control the microstructure; creep tests under compression and with four-point bending in the 1700-1900+°C temperature range will be used to determine effective diffusion coefficients.

2.5 Solid Solubilities in Silicon Carbide

Personnel: Professor R. L. Coble; J. Conwicke

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Intended measurements of the nitrogen solubility in silicon carbide has proven too formidable a problem to warrant continuation at this stage. Tests now are underway to conduct measurements of boron and phosphorous solubilities and their mutual solubilities.

2.6 Dislocation Velocities in $CaF_2$

Personnel: Professor R. L. Coble; R. Katz

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

R. Katz has followed the capability developed by Keig to measure dislocation velocities in calcium fluoride. Keig found that the apparent velocity for screw components was significantly higher than that for edge components. Katz has succeeded in isolating movements of the screw components and found them to be faster than the edges. He has also found that the screw components are more dependent upon the array of dislocations from which they emerge than are the edge components. Further clarification with respect to both dislocation arrays and impurity contents are underway.

3.0 Structure and Properties of Noncrystalline Solids

Personnel: Professors W. D. Kingery, C. J. Mogab, D. R. Uhlmann; T. J. Brown, D. S. Gelles, R. M. Hakim, W. T. Laughlin, J. H. Li, R. R. Shaw

3.1 Flow and Relaxation Processes in Simple Glass Forming Liquids

Personnel: Professor D. R. Uhlmann; W. T. Laughlin

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The phenomena of viscous flow, dielectric relaxation, and volume relaxation in simple glass-forming liquids are being investigated. Measurements of viscous flow in a $\alpha$-phenyl o-cresol, salol, and glycerine have been carried out over the range of viscosity from 10 to $10^{14}$ poise using bending-beam and falling-sphere viscosimeters. For $\alpha$-phenyl and salol the log $\eta$ vs $1/T$ relations were straight lines over the viscosity range from $10^5$ poise to the glass transition region, while for glycerine some curvature was noted at high viscosities. The implications of these results on various proposed theories of the glass transition are being explored.

Measurements of volume relaxation in glycerine have indicated behavior which cannot be described by a single relation time. Measurements on $\alpha$-phenyl and salol are presently being carried out.

3.2 Electrical Properties of Silicate Glasses

Personnel: Professor D. R. Uhlmann; R. M. Hakim

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The marked increase in resistivity which accompanies the partial substitution of one alkali ion for another in inorganic oxide glasses is termed the mixed-alkali effect. In order to elucidate the origin of this effect, measurements were carried out of the electrical conductivity and density of a series of simple silicate glasses in which $Rb^+$, $K^+$, $Na^+$, and $Li^+$ were partially substituted for $Cs^+$. When combined with electron microscopic observations, these measurements demonstrated that phase separation was not required for the occurrence of the mixed-alkali effect, and that no model suggested to date could provide an adequate description of the phenomena.

In attempting to provide such a description, measurements have been carried out of D.C. conductivity and dielectric relaxation in a series of single alkali silicate glasses, as well as of dielectric relaxation in the mixed-alkali (Cs-Rb, Cs-K, Cs-Na and Cs-Li) silicates.

In the binary glasses, the measurements of conductivity have been related to the occurrence of phase separation. The dielectric loss peaks are characterized by a distribution of relaxation times, and the forms of loss vs frequency relations are similar to those reported previously for $Na_2O$-$SiO_2$ and other glasses. The data on the mixed glasses are presently being analyzed.

## 3.3 Rapid Quenching of Nonmetallic Materials

Personnel: Professor D. R. Uhlmann; T. J. Brown

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The technique of splat-cooling (rapid cooling by propelling a molten sample onto a cold substrate) is being used to study nonmetallic materials. Particular emphasis is being placed on obtaining many materials as glasses which cannot ordinarily be obtained in the amorphous solid state. Initial studies have been concerned with some standard salts and simple molecular liquids, and in nearly all cases have resulted in the formation of glasses. In the case of water, an amorphous (by X-ray diffraction) phase was obtained which crystallized in the same temperature range as amorphous vapor-deposited samples.

## 3.4 Strength of Inorganic Oxide Glasses

Personnel: Professor D. R. Uhlmann; J. H. Li

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The strength of some simple inorganic oxide glasses is being investigated. Variables include size, composition, submicrostructure, drawing conditions, temperature, and time.

## 3.5 Cold Flow in Inorganic Oxide Glasses

Personnel: Professor D. R. Uhlmann; J. H. Li

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The "cold flow" phenomenon (anomalous flow in the glassy state at high stress levels) has been observed in several polymeric materials. To investigate the generality of this phenomenon, fibers of a borosilicate and a rubidium silicate glass have been tested in the $10^4$-$10^5$ psi range at temperatures between 20 and 50 degrees of their respective strain points. Measurements on the borosilicate glass for periods up to weeks in duration have indicated the absence of any anomalous flow. (No stress dependence of the viscosity was noted.)

In contrast, the viscosity of the rubidium silicate glass was found to decrease significantly with increasing stress at stress levels above about $3 \times 10^4$ psi. The variation of this stress level with temperature, as well as the detailed form of the strain rate vs stress relation in the high stress region are presently being investigated.

## 3.6 Effect of High Pressure on Glass

Personnel: Professor D. R. Uhlmann; T. J. Brown

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

A number of glasses have been shown to undergo a permanent densification when subject to high pressure. The variation of this densification with composition, temperature, and pressure has been investigated in a number of simple silicate systems. The effect of this compaction on the properties of the glasses is presently being studied, as is their subsequent annealing behavior.

## 3.7 Subliquidus Immiscibility and Property Anomalies in Alkali Borate Glasses

Personnel: Professor D. R. Uhlmann; R. R. Shaw

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The extent of subliquidus immiscibility in the Li, Na, K, Rb, and Cs borate systems has been determined with electron microscopic techniques. The consolute temperatures ranged from about 570°C in the $Cs_2O$-$B_2O_3$ system to about 660°C in the $Li_2O$-$B_2O_3$ system, while the consolute compositions were about 10 mole % alkali oxide in all systems except $Na_2O$-$B_2O_3$, where it was about 16 mole %.

Measurements have also been carried out of the density, refractive index, thermal expansion coefficient, elastic moduli and microhardness of glasses in each system. The property vs composition relations thus obtained were related to the observations of immiscibility and to other structural data on the glasses; and the nature of the so-called "boric oxide anomaly" has been explored.

The relation between phase separation and various properties of glasses is presently being explored further, and an attempt is being made to establish a relation between structural models and the thermodynamic parameters relevant to phase separation.

### 3.8 Electrical Properties of Chalcogenide Glasses and Crystals

Personnel: Professor D. R. Uhlmann; R. M. Hakim

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The effects of microstructure on the electrical properties of As-I-Te and As-Se-Te glasses, crystals, and glass-ceramics are being investigated. Measurements of D.C. conductivity, Hall effect, and Seebeck effect are being carried out and will be correlated with the results of electron microscopic observations.

### 3.9 Characterization of Microporosity in Vapor-Deposited Thin Films

Personnel: Professor C. J. Mogab

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The presence of a micropore phase in vapor-deposited thin films has been experimentally observed in several instances. This phase is generally undesirable as it detracts from optimal film properties and is likely to be responsible for numerous "aging" effects observed in various films. At the present time it appears that no detailed study of the mechanisms by which microporosity forms or the dependence of the amount and morphology of this phase on deposition parameters and residual vacuum level has been carried out.

A high vacuum ($5 \times 10^{-9}$ torr) ion-pumped system and a UHV oil-diffusion pumped system are being used to establish empirical quantitative relations between film density and deposition parameters. The systems are equipped with electron gun evaporation sources, deposition rate controllers, and mass spectrometers for residual gas analysis.

## 3.10 Annealing Kinetics in Noncrystalline Si, Ge, and SiC

Personnel: Professors W. D. Kingery and C. J. Mogab

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Semiconducting materials with crystalline modifications having a high degree of homopolar bonding and low coordination numbers can be obtained in a metastable noncrystalline state by vapor-quenching. Noncrystalline Si, Ge, and SiC all undergo an irreversible diminution of conductivity on annealing which has been attributed to the annihilation of acceptor like levels near the edge of the valence band whose origin is in the potential fluctuations caused by structural disorder.

The kinetics of the annealing process in noncrystalline SiC has been studied and was found to follow a logarithmic rate law consistent with thermally activated processes distributed in activation energy. Work is now under way to determine if a similar description can be applied to the annealing of conductivity changes in noncrystalline Si and Ge.

## 3.11 Amorphous to Crystalline Transition in Barium Titanate

Personnel: Professor W. D. Kingery; D. S. Gelles

Sponsorship: U.S. Atomic Energy Commission, AT(30-1)-3773, DSR 70112

A metastable phase of barium titanate has been prepared by a flame-spray technique using a Verneuil oxyhydrogen torch to melt a 20 micron particle-size powder of barium titanate which was then rapidly cooled by spraying into a liquid nitrogen bath.

The product showed amorphous X-ray and electron diffraction patterns. The major peak did not correspond to that of the barium titanate structure. The grain size, estimated from line broadening was 13 Å, the density was 4.72, the index of refraction was 2.005, the dielectric constant 18, the tan $\delta$ .002, up to 100°C where ionic conduction effects became apparent.

A transition to the crystalline phase began at 490°C with nucleation and growth to 200 to 350 Å of the barium titanate particles. Nucleation of $TiO_2$ or BaO particles also occurred. As the transformation proceeded, the dielectric constant increased. A delay time of 300 seconds was needed before the reaction at 500°C could proceed.

The crystalline structure resulting from heat treatment at 650°C for 10 hours consisted of $BaTiO_5$ grains, 200 to 350 Å in diameter. The index of refraction was 2.36, the density 5.77 gm/cm$^3$, and the dielectric constant rose to 65 and the loss dropped to .001 at room temperature.

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## IX. PROPERTIES OF POLYMERS

### Personnel

(All personnel from the Department of Metallurgy and Materials Science)

Professor D. R. Uhlmann, Assistant Professor
J. B. Park, Research Assistant
R. M. Kimmel, Research Assistant
T. J. Brown, Engineering Assistant

### Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75127

### Research Report

#### 1.0 Crystallization and Properties of Polymers

Personnel: Professor D. R. Uhlmann; J. B. Park, T. J. Brown

The effect of crystallization conditions on the morphology and properties of crystalline polymers is being investigated. The materials being studied initially are polyethylene and some of the important fiber-forming polymers.

#### 2.0 Crystallization and Properties of Polymers under Pressure

Personnel: Professor D. R. Uhlmann; R. M. Kimmel

The permanent changes produced in the properties of glass-forming amorphous polymers by various combinations of high pressure and temperature are being investigated, using a Bridgman anvil "squeezer" apparatus and a 200,000 psi gas apparatus. Permanent changes in polymer density are directly related to theories of the glassy state and the glass transition. In polymethyl methacrylate, a maximum densification of about 1.5% has been achieved by treatment at the glass transition pressure corresponding to a given temperature. At higher pressures, lower densifications are observed. The sequence of the pressure-temperature cycle has also been found to be important.

The kinetics of the annealing behavior of these densified polymers at one atmosphere and at temperatures below the glass transition are also being investigated and quantitatively analyzed. An attempt is being made to relate these results to hardness and other mechanical properties.

Crystallization of polymers under high pressure and changes in the properties of crystalline polymers with pressure treatment are being investigated using the Bridgman anvil and the gas apparatus, as well as a piston-cylinder solid medium press, soon to be completed.

## 3.0 Deformation of Amorphous and Crystalline Polymers

Personnel: Professor D. R. Uhlmann; J. B. Park, R. M. Kimmel

The deformation of amorphous and crystalline polymers is being investigated, with particular emphasis being placed on the cold flow phenomenon. In elucidating the relation between this phenomenon and the structure of the polymers, studies of the kinetics of recovery of the deformation are likewise being carried out.

## 4.0 Analysis of Time-Dependent Properties of Glass-Forming Systems

Personnel: Professor D. R. Uhlmann; R. M. Kimmel

A treatment in terms of distributions of activation energies is being developed and applied to the analysis of various time-dependent properties of glass-forming materials. These property changes include volume relaxation, time-dependent mechanical properties, and annealing of densified glasses. The results obtained by using this analysis are being related to various theories of the glassy state and glass transition phenomena. The analysis is being applied to data on low molecular weight organic materials and inorganic oxide glasses, as well as to high polymers.

# X. ELECTRONIC MATERIALS LABORATORY

## Personnel

(All personnel from the Department of Metallurgy and Materials Science except where indicated)

Professor H. C. Gatos, Professor
Professor A. F. Witt, Associate Professor
M. Lichtensteiger, DSR Research Staff
J. T. A. Pollock, DSR Research Staff
F. A. Kuznetsov, Visiting Scientist
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H. I. Andrews II, Research Assistant, Lincoln Laboratory
C. L. Balestra, Research Assistant
P. Bellin, Research Assistant
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G. T. Galyon, General Telephone & Electronics Fellow
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D. C. Johnston, Research Assistant
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L. Kiss, Graduate Student
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R. Singh, Research Assistant
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J. J. Stockler, Research Assistant, Lincoln Laboratory
T. M. Valahas, Research Assistant
W. J. Fitzgerald, Engineering Assistant
C. J. Herman, Engineering Assistant
T. W. Stewart, Technician
Susan E. Haroian, Secretary
Rachel A. Saxe, Secretary

Degrees Granted

K. Morizane, Sc.D., Metallurgy, January 1967
R. S. Mroczkowski, Sc.D., Metallurgy, June 1967
P. Tick, Sc.D., Metallurgy, June 1967
F. M. Roddy, E. E., Electrical Engineering, January 1967

Personnel who left during the period

V. Sadagopan, Research Associate (Now at AVCO, Everett, Massachusetts)
M. C. Lavine, DSR Staff (Now at Lincoln Laboratory)
D. F. Ellingwood, Technician (Now at NASA-ERC, Cambridge, Massachusetts)

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U. S. Atomic Energy Commission, AT(30-1)-3208, DSR 79878

Research Report

1.0 Compound Semiconductor Surfaces

Personnel: Professors H. C. Gatos, A. F. Witt; C. L. Balestra, T. M. Valahas

Sponsorship: Office of Naval Research and Advanced Research Projects Agency

Our research on the characterization of compound semiconductor surfaces this year was centered on GaAs and CdS.

Sinusoidal and pulsed field-effect experiments have been performed on etched A and B surfaces of n-type GaAs under various environmental conditions. The problem of electrical contacts on this material has been successfully solved by "sand blasting" the surfaces and by using In dots as solder at 500°C. In an alternative method we obtained satisfactory contacts by using tin and hydrazine monobromide as flux on freshly etched surfaces at 232°C.

In a large number of experiments we studied the dynamic behavior of surface states. The time constant of a surface state was determined from oscilloscope traces in the temperature range from 77°K to 430°K. The experiments were performed under a reduced pressure of $\sim 2 \times 10^{-5}$ torr in air and in an $O_3$ environment at atmosphere pressure. From the measured time constants for the transition of electrons from the surface state to the conduction band we could determine the position of a surface state $(E_c-E_t)$ with 0.51 eV. Under our experimental conditions no influence of the ambiant atmosphere on the time constant could be observed.

The investigation of the stationary behavior of surface states, (AC field effect) in the frequency range from 0.01 to 10 cps is currently being pursued.

Work on the characterization of CdS surfaces has been initiated. These experiments are performed in an ultra-high vacuum system under reduced pressures (minimum pressure obtainable $6 \times 10^{-12}$ torr). The vacuum system used is equipped with a mass spectrometer and automatic pressure control which by means of a back feeding circuit permits complete environmental control at any desired pressure and composition.

For the investigation of CdS surface characteristics we have developed a pressure decay calibration system. A special specimen holder permitting circulation of liquid nitrogen for low temperature work was designed and constructed. For investigations at elevated temperatures the specimen holder is heated by electron bombardment from an electron beam gun.

Initial experiments show that indium, the conventional contact material used on CdS is unsuitable because of excessive surface diffusion at the temperatures at which field effect experiments are performed. Indium has therefore been replaced by vapor deposited silver as contact material. Most recently pulsed field effect experiments were made on CdS wafers of 0.1 mm thickness. The measured room temperature time constant of the field effect decay was observed to be 10 milliseconds.

## 2.0 Crystallochemical Approach to Electronic Materials

Personnel: Professors H. C. Gatos, A. F. Witt; V. Sadagopan, P. Bellin, Daryl Carnam, N. Platakis, O. Sandven

Sponsorship: Advanced Research Projects Agency and National Aeronautics and Space Administration

Our crystallochemical approach, previously described, has been put to further use in correlating and developing new superconductors and semiconductors.

## 2.1 Superconductors

The critical current as a function of magnetic field has been experimentally determined for 40 representative compositions of the Ti-Nb-V ternary system. Fields up to 120 kilogauss were employed. The wire samples had been severely cold worked. This work complements the transition temperature measurements previously obtained on these samples. $T_c$ was observed to vary in a manner similar to $H_c$. The density of states as reflected by the electron to atom ratio appears as the dominant theoretical parameter. Resistivity data at 4.2°K and room temperature has been obtained. It is hoped that these measurements will indicate how the Bardeen-Cooper-Slichter interaction parameter varies with composition. The spread of critical current data indicates that current carrying capacity is extremely sensitive to impurities.

Critical currents ($J_c$) as high as $4 \times 10^3$ A/cm$^2$ at 80 Kgauss were observed. A current program of heat treatment will result in substantial increases in $J_c$. This will determine the suitability of these alloys as superconducting magnet materials.

Calculations of the specific heat parameter, $\gamma$, have been made using the Ginzburg Landau theory for type II superconductors.

Hardness measurements are being made to further characterize the system.

The current carrying capacity is thought to be related to the dislocation structure. Electron microscopy will be used to investigate this possibility.

A comparative study of the relationships between superconductivity and electronic structure in the transition metal carbides has been undertaken from an experimental and theoretical point of view. Electronic properties which relate to the energy band structure have been chosen to give information about the bonding in these materials, and to gain an understanding of the occurrence of superconductivity in some of the carbides, and to obtain parameters ($T_c$, N(0), $\theta_D$) which relate to a recently proposed two-band model of superconductivity for the transition metals and their alloys.

Specific heat measurements are being made in the range of temperature from 1-10$^{o}$K using a continuous warming method, in which heat is added to the sample at a constant known rate, and the subsequent rate of temperature increase is measured. The heat capacity is then obtained as

$$C = P/(dT/dt)$$

where P is the rate of heat input to the specimen, and dT/dt is the time rate of temperature increase. Using the continuous warming method it is possible to obtain high precision data in a relatively rapid manner.

Specific heat measurements have been made onthe following systems: TiC (single crystal), TiC, ZrC, HfC, VC, TaC, MoC and WC.

## 2.2 Semiconductors

The work on vitreous semiconductors is being continued with the systems $xAs_2Se_3 \cdot ySb_2Se_3$. The compounds are synthesized from the elements under vacuum and kept at a temperature of 750$^{o}$C for 24 hours. The resulting compounds have been analyzed by x-ray diffraction and were identified as glasses. The investigation of the temperature dependence of the resistivity revealed resistivity changes by a factor of $10^7$ for the temperature range from 23$^{o}$C to 300$^{o}$C. The resistivity was observed to decrease by a factor of ~ 3 for each 10% increase in $Sb_2Se_3$ in the system.

## 3.0 Distribution of Impurities in Solids

Personnel: Professors H. C. Gatos, A. F. Witt; L. Kimerling, R. Singh, D. Miller, L. Golovin

Sponsorship: Advanced Research Projects Agency, National Science Foundation, and the U. S. Atomic Energy Commission

Our investigation of semiconductor crystal growth characteristics and the distribution and incorporation of impurities is being continued. The recently developed technique for the measurement of instantaneous, microscopic rates of crystal growth by means of "rate striations" revealed that during Czochralski growth of semiconductor single crystals the actual rate of growth varies continuously and differs in some instances by order of magnitude from the pulling rate. It was found that the facet growth rate during rotational pulling is numerically identical with the pulling rate but the growth rate in the off-core region is subjected to continuous fluctuations the magnitude of which is determined by the extent of thermal asymmetry in the system, by the temperature gradient in the melt, by the rate of rotation and the rate of pulling.

An investigation of the effects of seed rotation on the uniformity of impurity incorporation revealed that at constant pulling rate the extent of back melting increases with increasing rotational rates up to about 40 rpm. Further increases of the rotational rate lead to a reduction of back melting because of homogenization of the thermal conditions in the melt. However rotational striations which reflect severe heterogeneities in impurity distribution are clearly visible at rotational rates up to 150 rpm. It is observed that crucible rotation is much more effective in eliminating non-rotational impurity striations and results in a better homogeneity of the impurity distribution.

In a series of experiments we investigated the extent of facet formation in InSb from a <111> direction. It was found contradictory to previous literature reports that it is uneffected by the presence of impurities. The extent of facet formation could, however, be controlled by the temperature gradient across the growing crystal and across the melt. It was also observed that the dislocation density is greatly influenced by the same temperature gradients.

An investigation of the effects of radiation damage on the electrical properties of germanium has recently been initiated. In the first part of this investigation antimony doped single crystal of germanium with low dislocation densities were grown by the Czochralski method. Small samples of this material were subsequently exposed to Co-60 $\gamma$-radiation in the irradiation facility of the Massachusetts General Hospital. The preliminary experiments indicate partial compensation due to the presence of radiation induced traps. An apparatus for the measurement of the minority carrier lifetime has recently been constructed. A setup for photoconductivity measurements is currently under construction. The above tools combined with Hall measurements and x-ray analyses will permit a detailed study of the behavior of carriers in the doped and irradiated material.

## 4.0 Semiconductor Growth

Personnel: Professors H. C. Gatos, A. F. Witt; M. Lichtensteiger, J. M. Harris, G. Galyon

Sponsorship: Advanced Research Projects Agency

Single crystal (111) beta silicon carbide has been grown expitaxially on (111) silicon substrates at 1150°C using a mixture of silane and propane and hydrogen. The quality of the films as revealed by x-ray analysis is good. The thin film single crystals exhibit, however, considerable variation in thickness which is attribtued to unfavorable gas flow conditions. Preliminary experiments indicate the simultaneous deposition of alpha and beta silicon carbide under conditions of increased growth rate. The deposition of SiC on to SiC substrates is being delayed because of the unavailability of a suitable susceptor material. At present experiments are carried out with Ti, TiC, and SiC as prospective susceptors.

The epitaxial deposition of PbSe by sputtering on to glass and sodium chloride substrate has been successful. X-ray analysis indicated single crystalline deposits of <111> orientation on both substrates. It was observed that p- and n-type PbSe can be obtained by varying the substrate temperature. The formation of p-n junctions in PbSe by this method is currently under investigation.

An investigation of the formation of III-V compound alloys in single crystal form has been initiated. Preliminary experiments were carried out with GaSb-InSb in a Czochralski system. Currently under construction is a setup by which Bridgman experiments can be carried out at elevated pressures (10 Kbar).

## 5.0 High Pressure Studies

Personnel: Professor H. C. Gatos; H. I. Andrews, G. Galyon

Sponsorship: Lincoln Laboratory

Progress continues on the phase relations and polymorphic transformations in the HgSe-HgS system.

Recent work in a liquid pressure-transmitting medium with manganin coil pressure gauge in situ has provided the most accurate data yet on the pressure of the zinc blend cinnabar transformation. A smooth and gradual decrease of transformation pressure as HgS content of the solid solution increases occurs up to at least 50% HgS by weight. HgSe transforms at 7.4 kilobars; the 50:50 alloy transforms at 3.4 kilobars. Similar measurements at temperatures of 125°C and 250°C show increased transformation pressures at all compositions with nearly parallel smooth and gradual decreases as HgS content increases. Further measurements to both higher compositions (approximately 60 weight percent HgS) and to higher temperature (about 400°C) are in progress.

In a solid pressure-transmitting medium, differential thermal analysis is yielding better data on the cinnabar to zinc blend transformation on heating at constant pressure at the mercury sulphide end of the diagram. The solid medium with its less well defined pressures must be employed because of the higher temperatures required for the transformation and the high pressures required to prevent decomposition of mercury sulphide rich alloys. Experiments using this technique are planned also for determination of melting points across the entire diagram.

The high pressure of cinnabar phase of the alloys may be stabilized at one atmosphere by quenching to liquid nitrogen temperature before releasing the applied pressure. The electrical resistance increases several orders on warming through the transformation giving the reverse transformation temperature. Studies of HgSe on slowly warming are complete.

## 6.0 Magnetic Resonance in Non-Metallic Spinels

Personnel: Professor H. C. Gatos; J. J. Stickler

Sponsorship: Lincoln Laboratory

Microwave resonance studies have been continued on $CoCr_2O_4$ (ferrimagnetic spiral), and additional spin resonance measurements have been made on $MnI_2$ (flat antiferromagnetic spiral). The spectra observed in powder samples of $CoCr_2O_4$ and single crystal samples of $MnI_2$ were measured as a function of frequency and temperature.

Neutron diffraction studies have shown that $CoCr_2O_4$ orders in a ferrimagnetic spiral below 31°K and has a Neel spin configuration between 86° and 96°K. The microwave spectra measured from the Neel temperature of 96°K to 4.2°K exhibit a sharp transition at the spiral ordering temperature of 31°K. Between 31° and 96°K, $CoCr_2O_4$ behaves ferrimagnetically with a net magnetization close to compensation. Two resonance modes were observed in this region, one identified as an exchange mode and the other as a uniform precession mode. The zero-field frequencies and effective g-factors for these modes were computed as a function of temperature using the molecular field calculations of Menyuk and Dwight. Excellent agreement with measured data was obtained. Computer calculations are now under way to calculate the frequencies of the correlated spiral modes corresponding to the resonance modes observed below 31°K.

Antiferromagnetic resonance has been observed in single crystals of $MnI_2$ at liquid helium temperatures and in the range of frequencies from 35 to 70 GHz. Neutron diffraction studies have shown that the $Mn^{2+}$ spins order in flat spiral spin configuration below 3.48°K and with a spin propagation vector along the (307) direction. The resonance data indicates the presence of appreciable short-range ordering at 4.2°K. At the lowest temperature reached by pumping on liquid helium, namely 1.5°K, the sample had a zero-field resonance at 48 GHz. At this temperature the resonance frequency varied almost quadratically with applied fields. Several weaker resonances were also observed at the lower temperatures; the origin of these lines is as yet uncertain. All the resonances exhibit some anisotropy with applied field which could be attributed to demagnetizing effects in the planar sample. A theoretical analysis of the resonance based on a modification of the calculations of Cooper et al is being attempted.

## 7.0 Niobium Oxide Single Crystals

Personnel: Professor H. C. Gatos; E. R. Pollard

Sponsorship: Lincoln Laboratory

A new technique for the growth of single crystals of high temperature materials has been perfected in conjunction with T. B. Reed of Lincoln Laboratory. The technique employs the well known cold hearth phenomenon of arc melting and as such avoids the problem of crucible contamination. The crystals are pulled in the Czochralski fashion from the resultant molten puddle.

Niobium monoxide single crystals have been grown in this furnace and its electrical properties have been investigated as a function of temperature and composition. The NbO single phase field was found to exist from 0.980 to 1.020±0.002 oxygen to niobium molar ratio. Niobium monoxide has metallic conductivity, ~5 x $10^4$ $(\text{ohm-xm})^{-1}$ at 300°K, is superconducting around 1.4°K, exhibits a slightly increasing magnetic susceptibility with decreasing temperature and increasing oxygen/niobium ratio. The Seebeck Coefficient and Hall constant indicate that the majority carriers are electrons with an effective carrier concentration (at O/Nb = 1) of about 0.4 electron per NbO molecule. The room temperature specular reflectivity was measured out to 12 eV, and Kramers-Kronig analysis has yielded the real and imaginary parts of the complex dielectric constant. The peaks in the imaginary component were correlated with interband transitions and a parameterized tight binding (Slater-Koster scheme) calculation to yield approximate values for band separations. Magnetoresistance measurements have been carried out at the National Magnet Laboratory in fields up to 150,000 gauss. Niobium monoxide exhibits anisotropic magnetoresistance as well as apparent magnetic breakdown at about 20 kG in the (100) direction. With (100) breakdown, all directions had a quadratic dependence on the magnetic field.

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P. A. Tick, "Condensation on Equilibrium Surfaces in Simulated Metal Systems", Sc.D. Thesis, June 1967.

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A. F. Witt, "Study of Impurity Heterogeneities in InSb by Means of a Permanganate Etchant", J. Electrochem. Soc. 114, 298 (1967).

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## XI. SUPERCONDUCTIVE MATERIALS

### Personnel

(Personnel from Department of Metallurgy and Materials Science except where indicated)

Professor J. Wulff, Professor
Professor R. M. Rose, Associate Professor
Professor L. Gruenberg, Assistant Professor, Electrical Engineering
T. H. Courtney, Research Associate
K. R. Comey, Teaching Assistant
S. Foote, Research Assistant
J. Hafstrom, Teaching Assistant
K. A. Jones, Research Assistant
M. L. A. MacVicar, NSF Trainee
D. Morrison, Research Assistant
J. Pearson, Teaching Assistant
G. Rauch, U. S. Steel Fellow
R. Ricketts, Teaching Assistant
B. P. Strauss, Research Assistant
S. Jackson, Student Assistant, Physics
B. R. Rose, Student Assistant
I. M. Puffer, Engineering Assistant
Phyllis M. Stratton, Secretary

### Degrees Granted

K. R. Comey, Jr., S.M., January 1967
B. P. Strauss, Sc.D., June 1967
M. L. A. MacVicar, Sc.D., September 1967

### Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75124
National Science Foundation, GK 1073, DSR 76350; GK 1071, DSR 76353
Office of Naval Research, Nonr 3963-16, DSR 74611

## 1.0 High-Field Solid Solution Superconductivity

Sponsorship: Advanced Research Projects Agency, National Science Foundation

### Research Report

### 1.1 Effect of Cold Work on Superconducting Current Density of a 40 wt.% Nb-Ti Alloy

Plastic deformation is effective in increasing the current density, $J_c$, of these alloys only when severe (ca. 90% R. A.). The critical field is quite sensitive to deformation in this particular alloy and interstitial oxygen does not improve the $J_c$ of cold-worked alloys. The influence of oxygen on $J_c$ of these wires may be explained by changes in the dislocation and martensite plates configuration with oxygen content.

### 1.2 Superconductivity and Aging in the Nb-Ti Systems

The response of $J_c$ to aging both cold-worked and recrystallized specimens with various oxygen contents, has been studied in this system. Optimum critical fields are found at roughly the 50 wt.% composition whereas optimum $J_c$ is found in alloys with slightly higher Ti content. Several properties, $\omega$ and $\alpha$, are both effective fluxoid pinners and the operative one is dependent on the composition, included oxygen content, of the alloy.

### 1.3 Yttrium, Lanthanide and Actinide Series Additions in Nb-Ti Alloys

Much higher $J_c$ values have been obtained by adding small amounts of Y, Gd, or Th to Nb-Ti alloys. These addition agents combine with oxygen during aging of the alloy to form an effective fluxoid dispersion. These alloys have the highest current densities of any alloys we have heretofore processed.

## 2.0 Superconductivity of the Transition Metals

Sponsorship: National Science Foundation

Research Report

We have found that the resistive critical field anisotropy of Nb wire may be altered by processing, particularly drawing, swaging and annealing. We are presently preparing a torsion experiment to test the hypothesis that such behavior is due to "internal surface" nucleation of superconductivity. The role of oxygen in Nb has also been somewhat clarified. The use of ultra-high vacuum has eliminated many spurious contamination effects, and analysis of the diffusion problem has enabled us to homogenize our materials. Ultrasonic and low angle x-ray scattering experiments are underway to test the clustering model. The vanadium tunneling research is also under way.

## 3.0 Electron Tunneling and Superconductivity of Niobium

Sponsorship: Office of Naval Research

Research Report

### 3.1 Tunneling into Nb Single Crystals

We have developed a reliable technique for the measurement of the energy gap in K-space. The gap for the <110> and <112>, and the average gap are all 3.10 mv. For <100>, the gap is 2.84 mv; for <111>, 3.19 mv, and for <311>, slightly more. The angular resolution is the best of any technique, and energy resolution is limited only by temperature and equipment. Low and high energy structure corresponding to multiple gaps has also been observed.

### 3.2 Tunneling in Alloys

The above-mentioned technique has been adapted for use on alloys. Initial experiments on 80% Nb-20% Ti have succeeded, but junction quality must be improved, as excess currents are still large.

## 4.0 Superconducting Composites

Sponsorship: Advanced Research Projects Agency

Research Report

Magnetic measurements have demonstrated the existence of a strong double proximity effect in the copper matrix of various Nb-Cu composites of similar geometry. The primary effect persists up to the resistive transition temperature. The secondary effect persists up to about $3^{0}$K.

Publications

L. Gunther and L. W. Gruenberg, "de Haas-van Alphen Oscillations in the Critical Temperature of Type II Superconductors", Sol. St. Comm. 4, 329 (1966).

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G. Beske, P. Hilsch and J. Wulff, "The Effect of Precipitation on Superconducting Properties of an Al-15% Zn Alloy", Trans. Met. Soc., AIME, 229, 890 (1967).

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L. C. Skinner II and R. M. Rose, "Improvements in the Floating-Zone Electron Beam Technique for the Group V Refractory Metals", in 2nd Int. Conf. on Electron and Ion Beam Science and Technology.

M. L. A. MacVicar and R. M. Rose, "Measurement of the Anisotropic Energy Gap in Nb Single Crystals", in Proc. Symposium on Physics of Superconducting Devices.

T. H. Courtney and J. Wulff, "Quaternary Solid Solution Superconductors", in Physics Letters.

B. P. Strauss and R. M. Rose, "Superconductivity of a Composite of Fine Nb Wires in Copper", to J. App. Phys.

M. L. A. MacVicar and R. M. Rose, "Superconducting Energy Gap of Thin Films", to App. Phys. Letters.

## XII. X-RAY AND ELECTRON OPTICS LABORATORY

### Personnel

(All personnel from Department of Metallurgy and Materials Science except where noted)

Professor R. E. Ogilvie, Professor
Professor T. O. Ziebold, Associate Professor of Nuclear Materials, Department of Nuclear Engineering
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J. L. Bomback, Instructor and Graduate Student
S. Duerr, Research Assistant
W. J. Duffin, Research Assistant
R. H. Frost, Instructor and Graduate Student
N. G. Koopman, Research Assistant
P. K. K. Nayar, Research Assistant
A. Pinella, Research Assistant
A. Saffir, D. D. M.
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J. Adario, Technician
Karen Luciani, Secretary

### Degrees Granted

J. L. Bomback, Sc.D., Metallurgy, June 1967
J. S. Duerr, S.M., Metallurgy, June 1967
W. J. Duffin, Sc.D., Metallurgy, June 1967
N. G. Koopman, Sc.D., Metallurgy, January 1967
P. K. K. Nayar, Sc.D., Metallurgy, June 1967
A. Pinella, S.M., Metallurgy, September 1967

### Sponsorship

U. S. Atomic Energy Commission, AT(30-1)-3134, DSR 79855
Wright Air Development Center, AF33(657)-8906, DSR 76347
National Aeronautics and Space Administration, NsG-496(part), DSR 74568

## Research Report

### 1.0 Phenomenology of Multicomponent Diffusion

Personnel: N. G. Koopman, P. K. K. Nayar

Sponsorship: U. S. Atomic Energy Commission

Diffusion experiments have been carried out at 1000$^{o}$K in the Cu-Ag-Au ternary. In order to confirm the correlation of Onsager's extension of Fick's Law to multicomponent diffusion and the dependency of the diffusion flux to the atomic mobility and chemical potential, extensive activity measurements have been carried out in the Cu-Ag-Au ternary. The activity measurements were made in a zirconia solid state galvanic cell.

Diffusion experiments have been made in the Ag-Cu-Zn and Ag-Al-Zn systems. The third component, zinc, was diffused into the alloy single crystals from the vapor phase. The crystals were bent to different radii around an axis parallel to the (211) to introduce different concentrations of edge dislocations. The influence of the dislocations was investigated by measuring the penetration of the zinc.

### 2.0 Metallographic Studies of Craters and Ejecta Produced by Hypervelocity Impact

Personnel: A. Pinella

Sponsorship: National Aeronautics and Space Administration

For many years hypervelocity impact experiments were carried out with the purpose of studying crater formation and the laws which predict this process. Other recent aspects that have been included in the study of hypervelocity impact are: the possible chemical changes produced in the deformed material and metallurgical transformations that may occur in the target or ejecta.

This particular study has dealt with the study of metal transport from the projectile to the target material and metallographic features of the deformed material around the crater. Craters have been formed with projectiles traveling at 19.2 km/sec., 8.8 km/sec. and 2.7 km/sec. Sections taken through a crater have been studied with the electron microanalyzer and the scanning electron microscope.

3.0 Scanning Electron Microscopy of Fatigue Specimens

Personnel: R. H. Frost

Sponsorship: Wright Air Development Center

A scanning electron microscope was built to study the topology of iron whiskers. This instrument is now being used to study the nature of fractured surfaces and in particular, the deformation bands and cracks developed during fatigue. The unique feature of this instrument is the greater depth of field and greater magnification over conventional light microscopy. It also has the desirable feature that it is not necessary to replicate the surface to be studied as in normal electron microscopy.

4.0 Scanning Electron Diffraction

Personnel: J. L. Bomback

An electron diffraction unit was modified so that the diffraction patterns can be displayed on an x-y recorder or an oscilloscope. This instrument has been used to follow the crystallization kinetics of amorphous films and the order-disorder transformations in $Cu_3Au$ films.

5.0 Study of Metallic Meteorites

Personnel: J. S. Duerr

Sponsorship: Smithsonian Astrophysical Observatory

A considerable amount of work has been done on the role of pressure, temperature, and time on the formation of the Wismanstatten pattern found in metallic meteorites. A cooling model with low internal pressure has been proposed for the development of the structures found in metallic meteorites. The plessite areas in metallic meteorites are now being studied with the scanning electron microscope. This instrument has enabled us to confirm the presence of martensite with a (259) habit plane.

## 6.0 Crystal Chemistry

Personnel: W. J. Duffin

Sponsorship: U. S. Atomic Energy Commission

This phase of research has been concerned with the factors which control the formation of Cll, C40, and C54 type structures. The pseudo-binaries $ReSi_2$-$TiSi_2$, $TiSi_2$-$TiSb_2$ and $ReSi_2$-$ReAl_2$ have been investigated taking into account space filling, atom sizes, electron atom ratio, and electron configuration.

## 7.0 The Effects of Diet on the Microstructure and Microcomposition of Teeth

Personnel: A. Saffir, L. Sutfin

Sponsorship: National Institute of Dental Research

The topology and chemistry of rats teeth are being studied with the aid of the scanning electron microscope and the electron microanalyzer. The aim of this work is to investigate the role of various minerals, that are introduced into the rats diet, on the structure of the teeth and how this might influence the dental caries rate. The distribution of flourine is of considerable interest in this work.

## Publications

Z. Ban and R. E. Ogilvie, "The Role of Iron in the Oxidation of Molybdenum Disilicide," Trans. AIME, 236, (12), 1738-1742 (1966).

D. B. Brown and R. E. Ogilvie, "An Electron Transport Model for the Prediction of X-ray Production and Electron Backscattering in Electron Microanalysis," J. Appl. Phys., 37, (12), 4429-4433 (November 1966).

R. E. Ogilvie, "Electron Microanalysis of Paint Samples from the Bersheh Sarcophagus," Applications of Science in Examination of Works of Art, Proceedings of the Seminar, September 1966, Museum of Fine Arts, Boston.

R. E. Ogilvie and T. O. Ziebold, "Ternary Diffusion in Cu-Ag-Au Alloys," Trans. AIME, 239, p. 942 (1967).

A. Saffir and R. E. Ogilvie, "The Effects of Diet on the Microstructure of Teeth," Proceedings of Second National Conference on Electron Microprobe Analysis, June 1967.

T. O. Ziebold, "Precision and Sensitivity in Electron Microprobe Analysis, Analytical Chemistry, 39, p. 858, July 1967.

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## XIII. CORROSION LABORATORY

### Personnel

(All personnel are from the Department of Metallurgy and Materials Science)

Professor H. H. Uhlig, Professor
Dr. Florian Mansfeld, Research Associate
Dr. Hans Bohni, Postdoctoral Fellow
E. W. Cook, Jr., Research Assistant
D. J. Duquette, Research Assistant
H. H. Lee, Research Assistant
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M. Talerman, Research Assistant
Constance C. Lowery, Secretary

### Sponsorship

Army Research Office-Durham, DA-31-124-ARO(D)-47, DSR 79341
Office of Saline Water, Grant 14-01-0001-1133, DSR 76416
Shell Companies Foundation, Inc., DSR 70186
American Iron and Steels Institute, DSR 70436

### Research Report

The main activities of the Corrosion Laboratory are currently concerned with:

#### 1.0 Pitting Corrosion

Measurements and interpretation of critical potentials below which corrosion pitting of stainless steels and other passive alloys is avoided. In particular, environmental and metallurgical variables are emphasized.

#### 2.0 Initial Oxidation Kinetics of Metals in the Thin Film Region

Gaseous pretreatment of copper leads to surface faceting which, depending on the gas and crystal face, has a major effect on thin-film oxidation behavior.

## 3.0 Mechanism of Stress Corrosion Cracking

Critical experiments to differentiate between the electro-chemical theory of crack propagation in metals and an alternative theory based on reduction of surface energy by adsorbed ions. Effect of galvanic coupling; measurements of critical potentials below which damage does not occur. Emphasis on stainless and carbon steels.

## 4.0 Mechanism of Hydrogen Cracking

An investigation of the effect of cold work on susceptibility of ferritic and martensitic stainless steels, and also carbon and low-alloy steels. In the carbon alloy series, variables include metal purity, inclusion count, metallographic structure, alloying additions (C, Ni, Co, Mn, Cr).

## 5.0 Mechanism of Corrosion Fatigue

Factors of the environment affecting fracture of 1015 carbon steel subject to reverse stress cycling at 1850 cycles/minute. Controlled variables include dissolved oxygen concentration, chloride concentration, pH, temperature, and applied potential.

## 6.0 Passivity in Copper-Nickel Alloys

Passivity begins at or above 38 atom % Ni (unfilled d band). Addition of zinc, which contributes 2 electrons/atom, raises this critical nickel content to predictably higher values. Ternary alloys of other electron donors, e.g. Al, Ga, Ge, Si, are being investigated in order to further establish the mechanism of passivity in alloys.

## Publications

W. W. Bradley and H. H. Uhlig, "Effect of Heating Single Crystal Copper in $H_2$ and $N_2$ on Thin-Film Oxidation Kinetics," J. Electrochem. Soc. 114, 669-673, July 1967.

## XIV. METALS PROCESSING - Casting and Solidification

### Personnel

(All personnel from Department of Metallurgy and Materials Science)

Professor M. C. Flemings, Associate Professor
T. Z. Kattamis, Research Associate
W. A. Brown, DSR Research Staff
P. R. La France, Technical Instructor
L. K. Bigelow, Research Assistant
W. E. Brower, Research Assistant
A. J. Campagna, Teaching Assistant
J. M. Coughlin, Research Assistant
J. Kaneko, Research Assistant
R. Mehrabian, Teaching Assistant
S. A. Metz, Research Assistant
F. R. Mollard, Research Assistant
M. Myers, Teaching Assistant
A. M. Reti, Research Assistant
S. N. Singh, Research Assistant
D. R. Spencer, Research Assistant
R. W. Strachan, Research Assistant
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R. A. Berry, Technician
A. Kariotis, Engineering Assistant
A. Barbara Rich, Secretary

### Degrees Granted

F. R. Mollard, Sc.D., Metallurgy, February 1967
R. W. Strachan, Ph.D., Metallurgy, February 1967
J. M. Coughlin, S.M., Metallurgy, February 1967
J. Kaneko, Sc.D., Metallurgy, August 1967

## Sponsorship

Army Materials Research Agency, DA-19-020-AMC-5443(X), DSR 78824
Army Materials Research Agency, DA-19-020-AMC-2231(X), DSR 79885
Army Materiel Command, DA-36-038-AMC-2943(A), DSR 74963
Office of Naval Research, NONR-3963(09), DSR 79988
Advanced Research Projects Agency, SD-90, DSR 78893
U. S. Steel Grant-in-Aid, DSR 79693
American Foundrymen's Society, DSR 70438
American Iron & Steel Institute, DSR 76379

## Research Report

Research is primarily concerned with liquid-solid transformations; a central aim of the research is to gain greater control over structure and properties of materials through control of solidification. Work is currently under way in the following areas.

### 1.0 Crystal Growth

Sponsorship: Advanced Research Projects Agency

Continuing progress has been made in establishment of the Metal Crystal Growth Facility as part of the Center for Materials Science and Engineering. Crystal growing units installed during the previous fiscal year are now in full operation. Two new power sources have been acquired and a variety of refinements of equipment on hand are under way or have been completed. These include construction of apparatus to permit casting levitation melted alloys in small ingot molds under inert atmosphere or or vacuum.

Research on crystal growth has included continuation of study of structure of crystals grown in a magnetic field, and study of growth of "composite" crystals. These programs are discussed below.

### 2.0 Effect of Fluid Flow on Structure; Composite Materials

Sponsorship: Office of Naval Research

Research is continuing on effect of fluid flow on structure of metal single crystals and of unidirectionally solidified eutectics. Convection is inhibited by application of a magnetic field and induced by crossed electric and magnetic fields. Significant improvement in perfection of the eutectic crystals is obtained by inhibiting convection.

In related work, two-phase alloys of non-eutectic composition are being grown under steep temperature gradient at slow rate and it is shown that two-phase "composites" are produced in which the second phase is lamellar or rod-like. These resemble lamellar eutectics but can be grown of compositions far removed from eutectic composition. Initial work has been on lead-tin alloys. Other current work is studying extension of this technique to alloys in systems containing a peritectic.

A new study has been initiated to study effects of extremely strong convection on solidification structures.

3.0 Growth Kinetics and Structure of Metals Solidified at Large Degrees of Undercooling

Sponsorship: Department of the Army, U. S. Steel Corporation

Primary aim of this study is to investigate effects of large degrees of undercooling (up to $300^{\circ}$C.) on structure and solute redistribution in metallic alloys. A secondary aim of the research is to develop improved methods for producing nonequilibirum structures (supersaturated and/or glassy structures) by rapid cooling of metallic melts.

Experimental work is currently on (a) bulk samples (approximately 100 grams) undercooled in glassy containers, and (b) levitated metal droplets. The levitated metal droplets are undercooled and dropped between two rapidly closing metal platens (i.e., "splat-cooled") before nucleation. It is shown that coarsening (i.e., "ripening") significantly alters solidification structures even at extremely rapid solidification rates.

4.0 Solute Redistribution

Sponsorship: Department of the Army

This program, now essentially complete, has been concerned primarily with solute redistribution in liquid and solid during dendritic growth. Computer programs have been formulated for determining extent of solid state diffusion to be expected during dendritic growth of binary alloys. Comparison of results with experiment has been excellent. Useful simplified mathematical expressions have also been formulated. Experimental and analytical work has also been conducted on more complex systems (e.g., ternary alloys).

## 5.0 Macrosegregation

Sponsorship: Department of the Army

This research comprises analytical and experimental study of macrosegregation (in ingot solidification). A general expression has been obtained for segregation caused by flow of solute-rich liquid to feed solidification and thermal contractions. It is shown that inverse segregation and centerline segregation can be understood as limiting cases of the analysis, and other types of segregation including macroscopic "banding" can result from the fluid flow. A factor of major importance in determining segregation that has not heretofore been considered is the direction of fluid flow with respect to solidification isotherms. Experiments agree qualitatively and quantitatively with analytical results.

## 6.0 Dendrite Morphology and Dendrite Arm Spacing

Sponsorship: Department of the Army

This program is part of a continuing study in our laboratory of dendrite structure, orientation, and grain size. Work during the last year has concentrated on factors influencing final dendrite arm spacing in cast alloys and it has been shown that coarsening ("ripening") exerts a major effect. Related work has been on details of dendrite structures in rapidly solidified aluminum alloys and directionally solidified tin alloys.

Technological interest in factors influencing dendrite structure, and particularly dendrite arm spacing, is high because of the strong influence of these factors on mechanical and other properties of cast materials (and wrought materials produced from cast ingots).

## 7.0 Inclusions

Sponsorship: Department of the Army, American Iron and Steel Institute

Several related activities are under way, designed to study the formation and growth of non-metallic inclusions in metal melts (especially in steel). Inclusion formation in the Fe-Si-O and Fe-S-O systems is being studied. Apparatus has been constructed to permit observation of dendritic growth and inclusion formation in metal melts during solidification. Alloys employed are low melting alloys; the solidification process is viewed microscopically using polarized light.

Inclusion formation is being studied in melts solidifying with essentially plane front. Finally, interaction of inclusions with solidifying dendrites is being studied by mechanical addition of "inclusions" to alloy melts.

## 8.0 Ultra-High Strength Aluminum Alloys

Sponsorship: Department of the Army

Influence of solidification heterogeneities on properties of wrought aluminum alloys are being studied in this program. It has been shown that by careful control of solidification structure significant improvements in properties of wrought aluminum alloys can be obtained (e. g., tensile strengths in excess of 115,000 psi are obtained in rolled sheet).

In related work, study is under way of feasibility of obtaining "composite" structures in aluminum alloys similar to those previously obtained in lead-tin alloys (see Item 2 above). Study of properties of composites so produced is planned.

## 9.0 Hot Tearing

Sponsorship: American Foundrymen's Society

A new program has been initiated on influence of solidification variables on "hot tearing" (tendency of alloys to rupture during solidification).

## Theses

F. R. Mollard, "Growth of Composites from the Melt", Sc. D. Thesis, Department of Metallurgy, January 1967.

R. W. Strachan, "A Technique for Levitation Melting, Undercooling and Splat Cooling of Metals and Alloys", Ph.D. Thesis, Department of Metallurgy, February 1967.

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J. Kaneko, "Effects of Convection on Structure of Metal Crystals", Sc.D. Thesis, Department of Metallurgy, August 1967.

Publications

M. C. Flemings, "Controlled Solidification", Strengthening Mechanisms, J. Burke, N. Reed, V. Weiss, Editors. Syracuse University Press, 1966 (Proceedings of the Twelfth Sagamore Army Materials Research Conference).

T. Z. Kattamis, M. C. Flemings, "Dendrite Structure and Grain Size of Undercooled Melts", Trans. Met. Soc., AIME, v. 236, 1966, pp. 1523-5132.

H. P. Utech, M. C. Flemings, "Thermal Convection in Metal Crystal Growth; Effect of a Magnetic Field", Crystal Growth, H. S. Peiser, Editor, Pergammon Press, 1967, pp. 651-658.

T. F. Bower and M. C. Flemings, "Formation of the Chill Zone in Ingot Solidification", Trans. Met. Soc. AIME, v. 239, 1967, pp. 216-219.

T. F. Bower and M. C. Flemings, "Structure of Dendrites at Chill Surfaces", Trans. Met. Soc., AIME, v. 239, Oct. 1967, pp. 1620-1625.

M. C. Flemings, G. E. Nereo, "Macrosegregation, Part I", Trans. Met. Soc., AIME, v. 239, Sept. 1967, pp. 1449-1461.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt, Part I", Trans. Met. Soc., AIME, v. 239, Oct. 1967, pp. 1526-1533.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt, Part II", Trans. Met. Soc., AIME, v. 239, Oct. 1967, pp. 1534-1546.

T. Z. Kattamis, J. M. Coughlin, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing of Aluminum-Copper Alloys", Trans. Met. Soc., AIME, v. 239, August 1967, pp. 1504-1511.

T. Z. Kattamis, M. C. Flemings, "Solidification of Highly Undercooled Castings", Trans. A.F.S., v. 75, 1967, pp. 191-198.

T. Z. Kattamis, U. T. Holmberg, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing and Grain Size of Magnesium-

Zinc Alloy", J. Inst. Metals. 1967, v. 75, pp. 343-347.

## Papers Accepted for Publication

M. C. Flemings, R. Mehrabian, G. E. Nereo, "Macrosegregation, Part II", accepted for publication, Trans. Met. Soc., AIME.

M. C. Flemings, G. E. Nereo, "Macrosegregation, Part III", accepted for publication, Trans. Met. Soc., AIME.

P. J. Ahearn, M. C. Flemings, "Dendrite Morphology of a Tin-Bismuth Alloy", accepted for publication, Trans. Met. Soc., AIME.

T. F. Bower, M. C. Flemings, "Double Orientation of Cast Structures", accepted for publication, Trans. A.F.S., v. 75, 1967.

M. C. Flemings, "Directional Solidification", Proceedings Fourteenth Sagamore Army Materials Conference, Syracuse University Press (to be published).

M. C. Flemings, "Application of Theory to Solidification of Large Castings and Ingots", Proceedings Joint Conference on the Solidification of Metals, Brighton, England, December 4-7, 1967 (to be published).

## Research Reports

M. C. Flemings, S. N. Singh, T. F. Bower, "Effects of Solidification Variables on the Structure of Aluminum Base Ingots", Annual Report Contract No. DA-19-020-ORD-5706(A), Frankford Arsenal, Contract Period June 1966-June 1967 (to be published).

T. Z. Kattamis, M. C. Flemings, "Solidification of Iron Base Alloys at Large Degrees of Undercooling", Interim Report, Contract No. DA-19-020-AMC-0231(X), Army Materials Research Agency, October 1965-October. 1966.

M. C. Flemings, R. V. Barone, H. D. Brody, "Investigation of Solidification of High Strength Steel Castings", Technical Report, Contract No. DA-19-020-ORD-5443(X), Army Materials Research Agency, Contract Period October 1965-October 1966.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt", Technical Report No. 2 to Office of Naval Research, November, 1966.

# SECTION D

## MATERIALS ENGINEERING

# I. PLASTIC DEFORMATION AND STRAIN HARDENING

## Personnel

Professor A. S. Argon, Associate Professor, Mechanical Engineering
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W. Henry, Instrument Maker, Mechanical Engineering
Sandramarie Grant, Secretary, Mechanical Engineering, (part time)

## Sponsorship

National Science Foundation Grant GK-596, DSR 76044

## Research Report

Based on the etch-pitting experiments of Brydges reported last year, a statistical theory was developed by Argon and East for the laminar deformation (easy glide) of copper. The theory starts with the assumption that the mutual elimination of screw dislocations by cross slip in easy glide produces segmented edge dislocations where long primary segments are separated by short segments, of random length less than $1.07\,\delta$ on the cross slip plane, where $\delta$ is the critical cross slip annihilation distance for opposite type screw dislocations. First the distribution of the density of primary segments of such edge dislocations is derived. This distribution function is then used to derive the probability of capture of segmented edge dislocations by multipoles; the probabilities of production and annihilation of sources resulting from partial capture of such dislocations by multipoles; and finally, the stress and strain dependence of the transmittable dislocation density. Using these results and a well known expression for dislocation velocity based on forest intersections, the stress-strain curve at constant strain rate is obtained by imposing a condition of constant dislocation flux. The resulting yield stress; strain hardening rate; temperature, strain rate, and orientation sensitivities of the flow stress and the strain hardening rate; together with other derivable quantities such as slip line lengths and depths agree reasonably well with experimental measurements.

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## Publications

A. S. Argon and G. East, "A Statistical Theory for Easy Glide", Proceedings of the International Conference on the Strength of Metals and Alloys in Tokyo, Trans. Japan Inst. Metals, in press.

A. S. Argon, W. T. Brydges, "Deformation of Copper in Easy Glide", submitted to the Phil. Mag.

W. T. Brydges, "The Dependence of Yield Stress on Forest Dislocation Density in Copper Single Crystals, Phil. Mag., 15, 1079 (1967).

W. T. Brydges, "Spark-Machining Damage in Copper Single Crystals", J. Inst. Met., 95, 223 (1967).

## II MECHANICS OF DUCTILE FRACTURE

### Personnel

Professor F. A. McClintock, Professor, Mechanical Engineering
R. M. N. Pelloux, Visiting Associate Professor, Mechanical Engineering
O. L. Bowie, Mathematics Consultant, Mechanical Engineering
H. Huff, Visiting Research Associate, Mechanical Engineering
A. S. Argon, Associate Professor, Mechanical Engineering
C. A. Berg, Associate Professor, Mechanical Engineering
A. D. Chitaley, Graduate Research Assistant, Mechanical Engineering
J. C. Carson, Graduate Research Assistant, Mechanical Engineering
K. Norris, Graduate Research Assistant, Mechanical Engineering
J. Joyce, Graduate Research Assistant, Mechanical Engineering
R. Lotz, Graduate Research Assistant, Mechanical Engineering
J. H. Williams, Graduate Research Assistant, Mechanical Engineering
R. Hodges, Undergraduate Assistant, Mechanical Engineering
C. Weissgerber, Undergraduate Assistant, Mechanical Engineering
R. Harrington, Undergraduate Assistant, Mechanical Engineering
R. Plotnick, Undergraduate Assistant, Mechanical Engineering
W. Henry, Instrument Maker, Mechanical Engineering (part time)
R. Leonard, Instrument Maker, Mechanical Engineering (part time)
Sandramarie C. Grant, Secretary, Mechanical Engineering (part time)

### Sponsorship

National Science Foundation, GK-1875X, DSR 70615

### Research Report

Distributions of stress and strain are being sought for the inclusions, phase boundaries, and holes where ductile fracture nucleates, as well as around the tip of a growing crack. These results are used to suggest fracture criteria that are being checked experimentally and are to be used to predict ductile fracture in structures and in metal processing.

## 1.0 Local Mechanisms of Ductile Fracture

Observations with the scanning microscope as well as an optical stereomicroscope confirm the remarkable similarity in fracture mechanisms of aluminum and its alloys, copper, and mild steel, all of which crack predominantly by hole growth although with a very wide range of hole sizes. Hole growth was remarkably symmetrical, indicating that homogeneous continum mechanics should be valid. The observed ductilities fall below those expected from continum mechanical analysis, apparently because of the statistical effects and the local shear strain concentrations due to instabilities. The growth of a single cylindrical hole in shear was observed to follow closely the value predicted from a continum solution obtained by numerical methods.

## 2.0 Fracture Criteria

Specimens have been designed and tested to give criteria for plane strain crack nucleation as a function of triaxiality.

Once cracks are nucleated, an appropriate criterion for their growth seems to require a statement of the boundary tractions exerted by the surroundings on a thin layer that is being split. In one limiting case it is essentially the strain in the layer that determines the stresses, in another it is the displacements, their gradients, and their curvatures. Analysis of crack growth requires the general intermediate case.

## 3.0 Crack Growth

Classical fully plastic solutions for notched specimens turn out to be remarkably useful for studying crack growth. The strains are finite around a growing crack, and geometrical features such as the crack opening angle and low cycle fatigue striation spacing have been related to the apparent crack ductility as determined fractographically.

In the elastic-plastic regime, a solution for steady state growth of Mode III shear cracks has been obtained, giving for the first time the residual stress and strain fields. An approximate elastic-plastic analysis has also been shown to predict the conditions under which the final fracture in a tensile test can or cannot be stabilized.

## 4.0 Analytical Methoas

For general solutions to problems in plastic flow, the two methods currently under development are based on adjusting displacements to minimize a scalar measure of the force unbalance, and superimposing dislocation dipole distributions to satisfy the yield criterion and flow rule. In the meantime, computer routines developed elsewhere are being used for those problems for which they are acceptable.

### Theses

H. E. Alpaugh, Jr., "Plastic Deformation of Holes in Shear," S.M. Thesis, Department of Mechanical Engineering, 1967.

K. C. Norris, "Strain in the Neck of a Tensile Specimen," S.M. Thesis, Department of Mechanical Engineering, 1967.

Robert Hodges, "An Experimental Study of Crack Growth Instability in Fully Plastic Tensile Specimens," S.B. Thesis, Department of Mechanical Engineering, June 1967.

### Publications

Discussion of "The Influence of Metallurgical Structures on the Mechanism of Fatigue Crack Propagation," by C. Laird, Symposium on Fatigue Crack Propagation, ASTM Annual Meeting, 1966.

"Ductile Fracture by Hole Growth in Shear Bands," with Saul M. Kaplan and C. A. Berg, International Journal of Fracture Mechanics 2, 1966.

Brief Note on Desk-Top Experiments on Dislocations, Metals/Materials Today 15, p. 20, 1967.

J. E. Neimark, "The Fully Plastic, Plane-Strain Tension of a Notched Bar," edited by F. A. McClintock, accepted by the Journal of Applied Mechanics.

F. A. McClintock, "Local Criteria for Ductile Fracture," accepted by the International Journal of Fracture Mechanics.

F. A. McClintock, "A Criterion for Ductile Fracture by the Growth of Holes," accepted by the Journal of Applied Mechanics.

F. A. McClintock, "On the Mechanics of Fracture from Inclusions," to be published in report of ASM Seminar on Ductility.

# III. PROPERTIES OF FIBER COMPOSITES

## Personnel

Professor J. Wulff, Professor, Metallurgy and Materials Science
Professor J. W. Mar, Professor, Aeronautics and Astronautics
Dr. L. A. Shepard, Research Associate, Metallurgy and Materials Science
P. W. Heitman, Graduate Student, Metallurgy and Materials Science
G. O. Garmong, Graduate Student, Metallurgy and Materials Science
Lt. R. W. Render, Graduate Student, Naval Architecture
Lt. H. C. Lewis, Graduate Student, Naval Architecture
Lt. W. L. Marsh, Graduate Student, Naval Architecture

## Degrees Granted

N. G. Perreira, S.B., Department of Metallurgy, June 1967
W. Pletsch, S.B., Department of Metallurgy, June 1967

## Sponsorship

Air Force Office of Scientific Research, AF 49(638)-1463

## Research Report

### 1.0 The Influence of Intermediate Phases at the Fiber-Matrix Interface on Mechanical Properties

Intermediate phases may frequently form and grow at fiber-matrix interfaces due to chemical interaction, particularly at elevated temperatures. The effects of a brittle boundary phase on the mechanical properties of a fiber composite are being studied in the Al-Mo fiber system where the fiber itself can be made either moderately ductile or brittle. Ductility of the composite is reduced both by the brittle compound and the surface irregularities on the fiber that result from compound growth. The composite strength is directly relatable to the unreacted fiber volume portion.

## 2.0 The Influence of Fiber Diameter and Matrix Spacing on Fiber Composite Strength

It is recognized that the strength of fiber composites should increase at small matrix spacings though there is little supporting experimental evidence to date. Composites of pure iron and copper are being prepared with copper matrix spacings of the order of a micron by the bundle and draw technique. Preliminary results on completely recrystallized samples indicate a noticeable strength improvement at matrix spacings below 0.1 mm.

## 3.0 The Properties of Directionally Solidified Rod-Like Eutectic Alloys

The directionally solidified Al-$Al_3Ni$ eutectic is one of a number of alloys which can be grown as a fiber composite, with spacing and $Al_3Ni$ fiber size controlled by the rate of growth. The alloy shows characteristic fiber composite strengthening in contrast to the ordinary random eutectic solidification. Previous work has shown some unusual deformation properties at high temperature which may be significant in the possible processing and application of this material. A program for the determination of the effects of strain rate and temperature on tensile properties is under way.

### Theses

N. G. Perreira, "The Interface Bonding of Al and Al-NbTi", S.B. Thesis, Department of Metallurgy, June 1967.

W. Pletsch, "The Strength of Thin Pb Brazed Cu Joints at 77$^{o}$K and Room Temperature:" S.B. Thesis, Department of Metallurgy, June 1967.

### Presentations

P. W. Heitman and T. H. Courtney, "The Effect of Fiber-Matrix Reaction on the Mechanical Properties of Al-Mo Fiber Composites", Presented at the Fall Meeting of the AIME, Oct. 1967, Cleveland, Ohio.

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## IV. PHYSICAL AND CHEMICAL PROPERTIES OF FIBERS AND POLYMERS

### Personnel

Professor S. Backer, Professor, Mechanical Engineering
Professor I. V. Yannas, Assistant Professor, Mechanical Engineering
Professor E. S. Gilfillan, Visiting Professor, Mechanical Engineering
Dr. E. I. Valko, Senior Research Associate, Mechanical Engineering
Dr. G. Egbers, Visiting Engineer, Mechanical Engineering
R. C. Sheldon, Instructor, Mechanical Engineering
Mrs. M. Chu, DSR Staff, Mechanical Engineering
Miss S. Dayhoff, DSR Staff, Mechanical Engineering
R. M. Kimmel, Research Assistant, Mechanical Engineering
F. DeS. Lynch, Graduate Student, Mechanical Engineering
H. R. Plonsker, GraduateStudent, Mechanical Engineering
D. H. Ender, Research Assistant, Mechanical Engineering
E. C. Ibe, Graduate Student, Mechanical Enginee ing
A. Maranci, Graduate Student, Mechanical Engineering
S. C. Dangel, Graduate Student, Mechanical Engineering
N. Sung, Graduate Student, Mechanical Engineering
S. Arghyros, Graduate Student, Mechanical Engineering
R. D. Wells, Graduate Student, Mechanical Engineering
C. Monego, Graduate Student, Mechanical Engineering
H. Patel, Graduate Student, Mechanical Engineering
D. Jilla, Graduate Student, Mechanical Engineering
Dorothy Eastman, Secretary, Mechanical Engineering
Consuelo Godfrey, Secretary, Mechanical Engineering

### Degrees Granted

D. H. Ender, Sc.D., Mechanical Engineering, June 1967
H. R. Plonsker, Sc.D., Mechanical Engineering, February 1968
F. DeS. Lynch, Sc.D., Mechanical Engineering, February 1968
S. Dangel, M.S., Mechanical Engineering, June 1967
R. C. Sheldon, M.S., Mechanical Engineering, February 1967
R. D. Wells, S.M., Mechanical Engineering, February 1967
N. Senturk, M.S., Mechanical Engineering, February 1967

C. Monego, M.S., Metallurgy, February 1967

Sponsorship

Department of Agriculture, 12-14-100-7650(72), DSR 75227
Allied Chemical Corporation
Beaunit Corporation
Burlington Industries, Inc.
Department of Commerce, CST-1170, DSR 75208
Derby Foundation
Camille and Henry Dreyfus Foundation
Instron Corporation
Charles T. Main Company
Maremont Foundation (Saco Lowell)
Monsanto Corporation
Phillips Petroleum Company
J. P. Stevens Company
West Virginia Pulp and Paper Corporation

## Research Report

### 1.0 Nonlinear Viscoelastic Behavior of Polymers

Personnel: Dr. G. Egbers; N. Sung

The aim of this investigation is to promote the phenomenological understanding of polymer behavior at high strains. The range of validity of approximations which have been shown to be useful in the region of small strains is under scrutiny in this study of a variety of amorphous and semi-crystalline polymers.

### 2.0 Optical and Spectroscopic Study of Polymers at High Strains

Personnel: Dr. I. V. Yannas, Dr. G. Egbers; S. Kornfeld

Relaxation processes such as whole-chain, chain-segment, or side-group motion are under observation in this investigation of highly strained glassy, amorphous polymers. Aspects of yielding and fracture are included in this program.

3.0 Physical Study of Certain Collagenous States

Personnel: Dr. I. V. Yannas; S. Arghyros

A physicochemical and engineering study of the mammalian protein, collagen, in a variety of physical states, with or without nonaqueous plasticizers is underway. One of the immediate aims of this work is the determination of certain crucial viscoelastic properties of collagen in sheet and fiber form. A preliminary detailed study of the denatured form of collagen, gelatin, has been completed and will serve as a guide in this project, the long-range goal of which is to evaluate collagen as a material for the fabrication of articles and components which will be useful in medical and industrial applications.

4.0 The Effect of the Degree of Crosslinking of Cotton Cellulose on the Absorption Equilibrium and Diffusion of Dyes

Personnel: Dr. E. I. Valko; E. C. Ibe

A study is being conducted on the rate of diffusion of direct dyes into cotton crosslinked to various degrees. The average molecular weight of cellulose between crosslinks was varied in a ratio of 1 to 15. An equation was derived for the rate of diffusion as a function of both concentration of due and molecular weight between crosslinks. The study continues with the aim of shedding light on the fine structure of polymers in uncross-linked and crosslinked state, as well as on the mechanism of diffusion in crosslinked systems.

5.0 Bending Mechanisms in Textiles

Personnel: Dr. S. Backer; A. Maranci, D. Jilla

This study seeks to clarify the effect of interfiber friction on the bending rigidity and bending hysteresis of twisted, woven, and knitted structures. Consideration is being given to the severe deformations which occur at fabric crease lines.

6.0 Storage and Retrieval of Textile Information

Personnel: Drs. S. Backer, E. I. Valko; Mrs. M. L. Chu, R. A. Roach,

R. C. Sheldon

A computerized retrieval system has been developed capable of providing multiple search strategies for the information seeker. The language control necessary for filtering of input and queries of the system is continuously updated with indexing experience. Future efforts will emphasize build up of the store so that a large scale industry-cooperative experiment can be run late in 1968.

## 7.0 Mechanics of Fiber Drafting

Personnel: Dr. S. Backer; H. Patel

The mechanics of roller drafting are being studied in a model drafting system. Emphasis is being given to the drafting of blends of different fibers with significantly varying mechanical properties.

## Theses

R. C. Sheldon, "Development of a Time Shared Storage and Retrieval System," M. S. Thesis, Department of Mechanical Engineering, February 1967.

R. D. Wells, "Patterns of Flow of Technical Information - A Study and A System Design Problem for the Textile Industry," S. M. Thesis, Department of Mechanical Engineering, February 1967.

C. Monego, "The Mechanics of Rupture of Cotton-Dacron Blended Yarns," S.M. Thesis, Department of Mechanical Engineering, February 1967.

N. Senturk, "Theory of Fiber Entanglement," M.S. Thesis, Department of Mechanical Engineering, February 1967.

D. H. Ender, "Yielding of Glassy Amorphous Polymers," Sc. D. Thesis, Department of Mechanical Engineering, June 1967.

H. R. Plonsker, "The Dynamics of Roller Drafting," Sc. D. Thesis, Department of Mechanical Engineering, February 1968.

F. DeS. Lynch, "A Finite Element Method of Viscoelastic Stress Analysis with Application to Rolling Contact Problems," Sc. D. Thesis, Department of Mechanical Engineering, February 1968.

S. Dangel, "Dynamics of Spinning," M. S. Thesis, Department of Mechanical Engineering, June 1967.

Publications

I. V. Yannas and A. V. Tobolsky, "Crosslinking of Gelatin by Dehydration," Nature, 215, 509 (1967).

I. V. Yannas, "Preliminary Design of Biomaterials for the Replacement and Repair of Tissue and Organs", Proc. Conf. Eng. Med. Biol. Boston, 1967.

I. V. Yannas and A. V. Tobolsky, "Stress Relaxation of Anhydrous Gelatin Rubbers", J. Appl. Polymer Sci., in press.

I. V. Yannas and A. V. Tobolsky, "High Temperature Transformations of Gelatin", European Polymer J., in press.

I. V. Yannas, "Isochronal Temperature-Concentration Diagram for a Polymer-Diluent System", J. Polymer Sci. A-2, in press.

E. I. Valko, "Theory of Dyeing," Encyclopedia of Polymer Science and Technology, Vol. 5, 345 (1966), J. Wiley and Sons, New York.

E. I. Valko, W. F. Olds, and H. Tovey, "Nonreactive and Coreactive Additives in Cotton Crosslinking," Textile Research Journal 37, 253 (1967).

E. I. Valko and P. J. Angelo, Jr., "Spinning of Cotton Yarns from Cross-linked and Untreated Fibers on the Woolen System and Their Performance in Winder-weight Fabrics,"Textile Research Journal 37, 600 (1967).

C. J. Gogek and E. I. Valko, "Control of Radial Distribution of Cross-Links in Cotton Fibers," Textilveredlung 2, 423 (1967).

S. Backer, E. I. Valko, and M. L. Chu, Thesaurus of Textile Terms, Second Edition, MIT, Cambridge, Mass. (in press).

S. Backer, "The Thesaurus as a First Step in an Information Retrieval System," Textile Institute and Industry, April 1967.

H. Plonsker and S. Backer, "The Dynamics of Roller Drafting, Part I. Drafting Force Measurement," Textile Research Journal (with Plonsker) 37, 673-687, 1967.

S. Backer, E. I. Valko, and M. Liang, "The Problems of Textile Information Retrieval," Textile Research Journal 37, 880-894 (1967).

R. C. Sheldon, R. A. Roach, and S. Backer, "Design of an On-Line Computer-Based Textile Information Retrieval System," Textile Research Institute, 38, 81-100 (1968).

C. Monego and S. Backer, "Tensile Rupture of Blended Yarns," Textile Research Journal (in press).

P. Popper and S. Backer, "Instrument for Measuring Bending Moment Curvature Relationships in Textile Materials," Textile Research Journal, (in press).

P. Jacobs and S. Backer, Journals of Interest to the Textile Industry, MIT, Cambridge, 1967.

## V. STRUCTURAL MATERIALS

### Personnel

Professor F. J. McGarry, Professor, Civil Engineering
Professor R. C. Jones, Associate Professor, Civil Engineering
Professor F. Moavenzadeh; Associate Professor, Civil Engineering
Professor R. B. Williamson, Assistant Professor, Civil Engineering
Professor A. E. Z. Wissa, Assistant Professor, Civil Engineering
Dr. M. H. Gradowczyk, Research Associate, Civil Engineering
R. Kuguel, Research Engineer, Civil Engineering
L. Szekessy, Research Engineer, Civil Engineering
A. M. Willner, Instructor, Civil Engineering
A. J. O'Neill, Technical Instructor, Civil Engineering
J. A. Alexander, Research Assistant, Civil Engineering
J. E. Ashton, Research Assistant, Civil Engineering
Juliet H. Ashton, Research Assistant, Civil Engineering
S. E. Blouin, Research Assistant, Civil Engineering
T. W. Bremner, Research Assistant, Civil Engineering
A. S. Carrara, Graduate Student, Civil Engineering
C. B. Doughty, Research Assistant, Civil Engineering
J. F. Elliott, Research Assistant, Civil Engineering
P. Forooton-Rad, Research Assistant, Civil Engineering
M. Fujiwara, Research Assistant, Civil Engineering
K. E. Fusch, Graduate Student, Civil Engineering
D. J. Hatfield, Graduate Student, Civil Engineering
D. R. Heerwagen, Research Assistant, Civil Engineering
O. G. Herrell, Graduate Student, Civil Engineering
E. I. Isibor, Research Assistant, Civil Engineering
L. B. Keat, Graduate Student, Civil Engineering
R. C. Laible, Graduate Student, Civil Engineering
F. V. Lawrence, Jr., Graduate Student, Civil Engineering
A. C. Lemer, Research Assistant, Civil Engineering
D. J. MacFadyen, Graduate Student, Civil Engineering
A. J. Mancera, Graduate Student, Civil Engineering
W. A. Maude, Graduate Student, Civil Engineering
C. R. Nelson, Research Assistant, Civil Engineering
J. Nemec, Jr., Research Assistant, Civil Engineering

D. E. Newman, Undergraduate Student, Physics
R. C. Novak, Research Assistant, Civil Engineering
E. F. Olster, Research Assistant, Civil Engineering
M. D. Oosterbaan, Research Assistant, Civil Engineering
D. D. Scarlett, Undergraduate Student, Physics
A. E. Smith, Graduate Student, Civil Engineering
J. E. Soussou, Research Assistant, Civil Engineering
J. N. Sultan, Research Assistant, Civil Engineering
E. Tazawa, Graduate Student, Civil Engineering
A. C. Wilfert, Research Assistant, Civil Engineering
W. H. Everett, Northeastern University Cooperative Student, Civil Engineering
M. Kupferman, Northeastern University Cooperative Student, Civil Engineering
W. R. Navin, Jr., Northeastern University Cooperative Student, Civil Engineering
N. S. Peterson, Northeastern University Cooperative Student, Civil Engineering
R. F. Quinn, Northeastern University Cooperative Student, Civil Engineering
M. Saint-Victor, Northeastern University Cooperative Student, Civil Engineering
J. Williams, Northeastern University Cooperative Student, Civil Engineering
W. E. Wood, Northeastern University Cooperative Student, Civil Engineering
F. L. Baird, Laboratory Assistant, Civil Engineering
H. M. Hencke, Laboratory Assistant, Civil Engineering
J. T. King, Technician, Civil Engineering
A. P. Rudolph, Jr., Machinist, Civil Engineering
R. E. Boyd, Administrative Assistant, Civil Engineering
Kathleen A. Brennan, Secretary, Civil Engineering
Laura H. Eanes, Language Assistant, Civil Engineering
Sue A. Gilles, Language Assistant, Civil Engineering
Cynthia I. Sorenson, Secretary, Civil Engineering
Marianne N. Stewart, Secretary, Civil Engineering
Mary R. Veeder, Language Assistant, Civil Engineering
Caroline G. Whitney, Secretary, Civil Engineering

## Degrees Granted

J. E. Ashton, Ph.D., Civil Engineering, February 1967
A. S. Carrara, S.M., Civil Engineering, September 1967
M. Fujiwara, S.M., Civil Engineering, February 1967
D. R. Heerwagen, S.M., Civil Engineering, February 1967
O. G. Herrell, C.E. and S.M., Civil Engineering, June 1967
E. I. Isibor, S.M., Civil Engineering, February 1967
L. B. Keat, S.M., Civil Engineering, September 1967
D. J. MacFadyen, S.M., Civil Engineering, February 1968
W. A. Maude, Mat. E., June 1967
J. Nemec, Jr., Ph.D., Materials and Structures, September 1967
A. L. Smith, C.E. and S.M., Civil Engineering, June 1967
J. N. Sultan, S.M., Civil Engineering, February 1968

## Sponsorship

Listed under subheadings.

## Research Report

### 1.0 Brittle Fracture in Rocks and Portland Cement Concrete

### 1.1 Brittle Fracture in Rock

Personnel: Professors F. J. McGarry, R. B. Williamson and F. Moavenzadeh; E. I. Isibor, P. Rad, C.R. Nelson, M. D. Oosterbaan, and A. C. Lemer

Sponsorship: U.S. Department of Commerce, Northeast Corridor Transportation Project, C85-65, DSR 76103

The purpose of this study is to find physical or chemical means of reducing the energy and maximum stress necessary to fracture rock materials. Fracture surface work values have been measured for granite, marble, gneiss and schist using a stable cracking flexural test. Load-deflection curves have been recorded and the work expended to cause failure has been calculated. The extent of side cracking has been measured by quantitative microscopy and is used to calculate a corrected fracture work.

The addition of dilute aqueous solutions of surface active agents and certain salts has been found effective in decreasing both the maximum stress and the total work necessary to fracture the sample. A one percent aqueous solution of aluminum chloride at 90°C produces a fifty percent reduction in the fracture surface work, compared to the room temperature dry condition.

Thermal cycling of standard samples of each of the rocks is found to cause extensive cracking, and the resulting decrease in strength can be measured. The heat treatments are given at 540°C, 1280°C and 1800°C for one, five and ten cycles. Generally, the first heating cycle accomplished a major portion of the damage

A 1000-watt continuous operation $CO_2$-N-He gas laser has been employed to subject the rock samples to high fluxes of infrared radiation. This substantially weakens the rock after a few seconds of exposure. Extensive macroscopic cracks have been observed after thirty to sixty seconds of irradiation.

## Related Academic Subjects

1.41 Strength of Structural Materials

1.46 Portland Cement Concrete

## Theses

E. I. Isibor, "Effects of Chemical Environment on Rock Fracture," S.M. Thesis, Department of Civil Engineering, February 1967.

## Publications

F. Moavenzadeh, R. B. Williamson and A. E. Z. Wissa, "Rock Fracture Research," Publication R66-56, Civil Engineering, MIT, November 1966.

F. Moavenzadeh, R. B. Williamson and F. J. McGarry, "Report on Laser Assisted Rock Fracture," Publication R67-3, Civil Engineering, MIT, January 1967.

R. B. Williamson, F. Moavenzadeh and F. J. McGarry, "Laser Assisted and Chemically Assisted Rock Fracture," Procs. 9th Congress, Intl. Bureau for Rock Mechs., Leipzig, Germany, October 1967.

## 1.2 Brittle Fracture in Concrete

Personnel: Professor F. Moavenzadeh; A. J. Mancera, L. B. Keat, C. B. Doughty, T. W. Bremner

Sponsorship: Ford Foundation, DSR 76393

The purpose of this study is to provide a fundamental knowledge of the mechanism of fracture of brittle materials and its application to the understanding of the strength of portland cement concrete. It is anticipated that such a study will eventually lead to the development of a more rational method of design of concrete structures, and to the manufacture of better quality concrete.

### Related Academic Subjects

1.40 Introduction to Electron Microscopy
1.41 Strength of Structural Materials
1.44 Cementitious Materials
1.46 Portland Cement Concrete

### Theses

L. B. Keat, "Fracture of Concrete," S.M. Thesis, Department of Civil Engineering, September 1967.

## 2.0 The Solidification of Crystalline Polymers

Personnel: Professors R. B. Williamson and F. J. McGarry

Sponsorship: Manufacturing Chemists' Association, DSR 79545

The mechanical behavior of polymers is strongly dependent on the morphology and distribution of any crystalline regions. Further, crystallization is observed to occur during deformation and is the cause of the tear resistance on some polymers. This research is devoted to investigating the morphology and microstructure of crystalline polymers. The morphology of polymers solidified from a flowing melt has been of particular interest. The formation of external crystalline fibers in a flowing polymer melt has been hypothesized by A. Keller. These fibers have been shown to have an overgrowth of lamellar crystals. The fiber with its chain-folded lamellar crystals is called the shish kebab structure.

Related Subjects

1.40 Introduction to Electron Microscopy
1.471 Mechanical Behavior of Plastics

Publications

R. B. Williamson and R. Novak, "Fibrous-Lamellar Microstructure in Polyethylene," J. Polymer Sci. 5, 1967.
R. B. Williamson and W. F. Busse, "Intercluster Links - A Mechanism for Flow-Induced Crystallization of Polymer Melts," Bulletin of the American Physical Society 12, March 1967.
R. B. Williamson and W. F. Busse, "Flow-Induced Crystallization of Polymer Melts," J. Appl. Phys. 38, October 1967.

3.0 The Morphology of Hydrated Cements

Personnel: Professor R. B. Williamson; O. G. Herrell, A. E. Smith, A. C. Wilfert, E. Tazawa

Sponsorship: The Dow Chemical Company, DSR 70243

The hydration of portland cement is a solidification process that shares many characteristics with the solidification of other materials such as metals or polymers. One objective of this research is to observe the microstructure of portland cement and to determine the morphology of the hydrated components. Another objective is to determine the relationship between structure and properties and, finally, to be able to control properties by controlling the microstructure.

Related Academic Subjects

1.41 Strength of Structural Materials
1.44 Cementitious Materials
1.45 Structural Design of Pavements
1.46 Portland Cement Concrete

Theses

O. G. Herrell and A. E. Smith, "The Effects of Glycolic Acid and Dow Latex 464 (Saran) on the Strength and Microstructure of Neat Paste," C.E. Thesis, Department of Civil Engineering, June 1967.

Publications

O. G. Herrell, A. E. Smith, F. Moavenzadeh, and R. B. Williamson, "The Effects of Glycolic Acid and Dow Latex 464 (Saran) on the Strength and Microstructure of Neat Cement Paste," Publication R67-53, Civil Engineering, MIT, October 1967.

4.0 The Relationship Between Microstructure and Mechanical Properties of Cementitious Materials

Personnel: Professors R. B. Williamson and F. J. McGarry; C. B. Doughty

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 78898

The objective of this research is to control the process of hydration of portland cement in order to improve the properties of portland cement concrete. The nucleation (and/or multiplication) and growth of the hydration products are being studied using model systems and the electron microscope on actual samples of portland cement. Most of the electron microscopic techniques used in the past have not had a realistic water:cement ratio, but these studies have utilized new techniques that limit the amount of water necessary to hydrate the sample.

Related Academic Subjects

1.40 Introduction to Electron Microscopy
1.44 Cementitious Materials
1.46 Portland Cement Concrete

Publications

None

## 5.0 Fibrous Glass Reinforced Plastic Composites

Personnel: Professor F. J. McGarry; R. C. Novak, A. M. Willner, M. Fujiwara, J. N. Sultan

Sponsorship: Air Force Systems Engineering Group, Materials Laboratory, AF 33 (615)-2712, DSR 74969
The Dow Chemical Company, DSR 70243

### 5.1 Microcracking in Fibrous Glass Reinforced Plastics

Study of the parameters controlling microcracking under cyclic loading. Methods of crack detection, measurement. Effects of imposed stress level, number of cycles, orientation of reinforcing fibers, spacing of fibers. Loss of elastic and strength properties. Methods to toughen cross-linked resin matrices to prevent microcracking. Micromechanics of toughened resins, molecular flow phenomena. Relationships between microstructure of toughened resins and their resistance to crack propagation.

### 5.2 Matrix-Fiber Stress Transfer Mechanisms

Study of stress transfer details in glass fiber-resin composite systems. Direct experimental method to evaluate effects of aspect ratio, glass finish treatments, cyclic loading, exposure to water and toughened resins. Analysis of stresses at ends of fibers, as influenced by geometric details of fiber ends.

### Related Academic Subjects

1.42 Structural Materials
1.471 Mechanical Behavior of Plastics
1.472 Composite Materials

### Theses

M. Fujiwara, "Resin-Fiber Load Transfer in Fiber-Reinforced Plastics," S.M. Thesis, Department of Civil Engineering, January 1967.

J. N. Sultan, "Crack Propagation Behavior of Toughened Polyesters," S.M. Thesis, Department of Civil Engineering, September 1967.

A. S. Carrara, "The Effect of Fiber End Geometry on the Stresses in a Resin-Glass Composite," S.M. Thesis, Department of Civil Engineering, September 1967.

## Publications

F. J. McGarry, "Relationships Between Resin Fracture and Composite Properties," Progress Report submitted to Air Force Systems Engineering Group, Materials Laboratory, Air Force Systems Command, September 1966.

F. J. McGarry, "Crack Propagation Studies in Crosslinked Polymers," Progress Report submitted to Air Force Systems Engineering Group, Materials Laboratory, Air Force Systems Command, September 30, 1966.

F. J. McGarry, "Crack Propagation Studies in Fiber Reinforced Plastic Composites," Publication P66-5, Civil Engineering, MIT, October 1966.

A. M. Willner and F. J. McGarry, I. "Crack Propagation Resistance of a Rubber Modified Epoxy Resin," II. "Tensile Fatigue of Pure and Rubber Modified Epon 828 Resin," III. "Stress Induced Cracking in Graphite Fiber Reinforced Epoxy Resins," Progress Report submitted to Air Force Systems Engineering Group, Materials Laboratory, Air Force Systems Command, December 31, 1966.

M. Fjuiwara, "Resin-Fiber Load Transfer in Fiber-Reinforced Plastics," Publication R67-8, Civil Engineering, MIT, February 1, 1967.

F. J. McGarry, "Crack Propagation in Fiber Reinforced Plastics Composites," Conference on <u>Fundamental Aspects of Fiber Reinforced Plastic Composites</u>, Dayton, Ohio, May 24, 1966, sponsored by The Nonmetallic Materials Division, Air Force Materials Laboratory, January 1967.

F. J. McGarry and A. M. Willner, "Plastic Flow in Thermoset Polymers," Bulletin of the American Physical Society <u>12</u>, March 1967.

F. J. McGarry and A. M. Willner, "Microcracking in Fibrous Glass Reinforced Resin Composites," American Chemical Society Polymer Preprints, Vol. 8, Chicago, September 1967.

A. S. Carrara and F. J. McGarry, "The Effect of Fiber End Geometry on the Stresses in a Resin-Glass Composite," Publication R67-43, Civil Engineering, MIT, September 1, 1967.

## 6.0 Viscoelastic Analysis and Characterization

### 6.1 Viscoelastic Analysis of Multi-Layer System

Personnel: Professor F. Moavenzadeh; J. E. Ashton, J. F. Elliott

Sponsorship: Massachusetts Department of Public Works and U.S. Bureau of Public Roads, DSR 70087

This project is concerned with the analysis of a three-layer linear viscoelastic half-space under a uniformly distributed circular load. Such an analysis is an essential step in the development of a rational method of design for flexible pavements.

The solutions are being obtained for stresses and displacements at any point within the half-space. These solutions are obtained by replacing the elastic constants in the elastic solution by integral operators derived from the hereditary form of the linear viscoelastic constitutive equations.

#### Related Academic Subjects

1.45 Structural Design of Pavement
1.47 Mechanics of Materials
1.472 Composite Materials
1.473 Viscoelasticity

#### Theses

J. E. Ashton, "Stresses and Displacements in Viscoelastic Bodies," Ph.D. Thesis, Department of Civil Engineering, February 1967.

Publications

J. E. Ashton and F. Moavenzadeh, "Analysis of Stresses and Displacements in a Three-Layered Viscoelastic System," Proceedings 2nd International Conference on the Structural Design of Asphalt Pavements (Preprint Volume), 1967.

W. H. Perloff and F. Moavenzadeh, "Deflection of Viscoelastic Medium Due to a Moving Load," Proceedings 2nd International Conference on the Structural Design of Asphalt Pavements (Preprint Volume), 1967.

F. Moavenzadeh and J. E. Ashton, "Analysis of Stresses and Displacements in a Three-Layer Viscoelastic System," Publication R67-31, Civil Engineering, MIT, August 1967.

J. E. Ashton and F. Moavenzadeh, "Stresses and Displacements in Viscoelastic Bodies," Publication R67-9, Civil Engineering, MIT, February 1967 (Microfiche).

6.2 Viscoelastic Characterization of Sand Asphalt Mixtures

Personnel: Professor F. Moavenzadeh; J. E. Ashton, J. E. Soussou

Sponsorship: Massachusetts Department of Public Works and U.S. Bureau of Public Roads, DSR 70088

The long term goal of this study is to develop a rational method for the design of asphaltic pavement mixtures using principles based upon theories of viscoelasticity. To achieve this a systematic viscoelastic approach, similar to that applied to the analysis and design of solid rocket fuels and filled polymeric systems is being used.

Related Academic Subjects

1.45 Structural Design of Pavements
1.47 Mechanics of Materials
1.473 Viscoelasticity

Publications

F. Moavenzadeh and J. E. Soussou, "Final Report on the Viscoelastic Analysis of Sand-Asphalt Mixtures," Publication R67-32, Civil Engineering, MIT, August 1967.

## 6.3 Viscoelastic Characterization of Portland Cement Paste

Personnel: Professor F. Moavenzadeh; J. Nemec

Sponsorship: Ford Foundation, DSR 76393

This project examines the time dependent behavior of hydrated portland cement paste. The material is tested in creep and in stress relaxation to determine the limits of linear viscoelasticity and the influence of aging of the cement upon these limits.

The characterization thus obtained is thus utilized in a case of stress analysis using computer techniques within the theory of linear viscoelasticity.

### Related Academic Subjects

1.44 Cementitious Materials
1.46 Portland Cement Concrete
1.47 Mechanics of Materials
1.473 Viscoelasticity

### Theses

J. Nemec, Jr., "Viscoelastic Study of Cement Paste," Ph.D. Thesis, Department of Civil Engineering, June 1967.

## 6.4 Viscoelastic Analysis of Moving Load on Multi-Layer Systems

Personnel: Professor F. Moavenzadeh; Dr. M. H. Gradowczyk; J. F. Elliott

Sponsorship: U.S. Department of Transportation, Highway Administration, Bureau of Public Roads, DSR 70604

To develop a numerical technique for solutions of stresses and displacements on three-layer viscoelastic systems subjected to slowly moving load on the surface.

Related Academic Subjects

1.45 Structural Design of Pavements
1.47 Mechanics of Materials
1.471 Mechanical Behavior of Plastics
1.473 Viscoelasticity

Publications

None

## 7.0 Structural Metals and Metallic Composites

### 7.1 Structural Metals

Personnel: Professor R. C. Jones; F. V. Lawrence, W. A. Maude, D. R. Heerwagen, D. E. Newman, W. H. Everett, W. R. Navin

Sponsorship: Inter-American Program in Civil Engineering: Ford Foundation, DSR 76392
Advanced Research Projects Agency, SD-90, DSR 78898

#### 7.1.1 Cyclic Loading Effects

Study of dislocation arrangements in single crystals of bcc metals as a function of stress level and number of cycles. Constant stress amplitude tests in reversed flexure. Transmission electron microscopy on thin foils cut from test specimens by spark machining. Relation of subgrain structure to macroscopic and microscopic observations.

#### 7.1.2 Loading Rate Effects

Study of macroscopic and microscopic effects of rate of loading in single crystals of high purity iron. Load-deformation observation and work-hardening rate changes as a function of loading rate and crystal orientation. Dislocation arrangements, observed by transmission electron microscopy, related to macroscopic observations.

### 7.1.3 X-ray Topography

Application of Schultz X-ray topography techniques to observation of effects of early stages of plastic deformation in metal single crystals. Correlation of topographs with macroscopic strain measurements and microscopic deformation evidence.

#### Related Academic Subjects

1.02 Engineering Materials
1.40 Introduction to Electron Microscopy
1.41 Strength of Structural Materials
1.42 Structural Materials
1.43 Structural Properties of Metals

#### Theses

W. A. Maude, "X-ray Diffraction Topography of As-Grown and Deformed Alpha-Iron Single Crystals," Mat. E. Thesis, Department of Civil Engineering, June 1967.

#### Publications

D. R. Heerwagen, "Strain Rate Effects in Alpha-Iron Single Crystals," Publication R66-41, Civil Engineering, MIT, September 1966.

W. A. Maude, R. C. Jones and R. B. Williamson, "X-ray Diffraction Topography of As-Grown and Deformed Alpha-Iron Single Crystals," Publication R67-18, Civil Engineering, MIT, May 1967.

### 7.2 Metallic Composites

Personnel: Professor R. C. Jones; D. J. Hatfield, D. D. Scarlett, D. J. MacFadyen, K. E. Fusch, E. F. Olster

Sponsorship: Dow Chemical Company, DSR 70243

7.2.1 Structural Applications

Study of the directionality of fiber reinforced metal matrix composites to determine the degree to which the material is inherently anisotropic. Implications of such anisotropy on the structural analysis and design process. Study of mechanism for transferring stresses across joints in structures fabricated from metal matrix composites. Includes both experimental and analytical components.

7.2.2 Mechanics of Deformation

Experimental study of stress transfer, and fracture initiation and propagation characteristics in metal matrix composite systems. Fabrication and mechanical testing of limiting cases and model systems. Study of stress distributions in loaded composites and breakup of reinforcement at high deformations. Scanning electron microscopy of fracture surfaces.

Related Academic Subjects

1.42 Structural Materials
1.43 Structural Properties of Metals
1.472 Composite Materials

Theses

D. J. MacFayden, "Structural Aspects of Metal Matrix Composites," S.M. Thesis, Department of Civil Engineering, September 1967.

Publications

R. C. Jones, "Deformation of Wire Reinforced Metal Matrix Composites," Publication P67-10, Civil Engineering, MIT, June 1967.

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## VI. SURFACE PROPERTIES AND BEHAVIOR OF MATERIALS SURFACE LABORATORY, DEPARTMENT OF MECHANICAL ENGINEERING

### Personnel

Professor B. G. Rightmire, Professor, Mechanical Engineering
Professor E. Rabinowicz, Professor, Mechanical Engineering
Professor P. Gould, Assistant Professor, Mechanical Engineering
Professor W. D. Syniuta, Assistant Professor, Mechanical Engineering
S. Malkin, Research Assistant, Mechanical Engineering
C. Corrow, Research Assistant, Mechanical Engineering
R. McIntire, Research Assistant, Mechanical Engineering
Angela Theodore, Secretary, Mechanical Engineering

### Degrees Granted

J. D. Vitkauskas, Nav. Eng., June 1967

### Sponsorship

Pratt and Whitney Division of United Aircraft, DSR 70581
The Norton Company, DSR 76056
Sloan Basic Research Fund

### 1.0 Behavior Under Mechanical Stress of Adsorbed Layers on Tungsten Wire

Personnel: Professor B. G. Rightmire

Sponsorship: Unsponsored

### Research Report

The ultimate lubrication of an interface is provided by a monolayer of adsorbed molecules. Adsorption at a solid-solid interface thus has important technical applications.

A study is being made of physisorption at an interface each surface of which consists of a monolayer of oxygen chemisorbed to a tungsten substrate. The amount of coverage is estimated from the specific interfacial electrical conductance, which ranges from $10^8$ mho/cm$^2$ for the oxygen surfaces above, down to $10^5$ mho/cm$^2$ for one complete physisorbed monolayer sandwiched between the oxygen surfaces. Identical, electropolished tungsten wires are crossed and loaded normal to the circular, Hertzian contact area. The test liquid is allowed to drip steadily on the crossing of the wires, thus continually bathing with fresh liquid the contact and adjacent regions. A slow, oscillatory, relative sliding motion is imposed on the wires, so that conditions of equilibrium adsorption may be approximated at each end of a stroke. Electric current is controlled to give an interfacial potential drop on the order of 100 microvolts. All tests so far have been at room temperature.

Experimental values of specific conductance averaged over the contact area fall within the limits stated above for all liquids examined. Values depend strongly on the nature of the liquid molecules and on the maximum Hertz stress. Reproducibility is good for different spots of contact, whether obtained by relative displacement of the wires, by repolishing, or by use of a different pair of wires (the pair diameter may differ from that of the first pair).

A theory based on the assumption of thermodynamic equilibrium at the interface yields the conductance as a function of load, for a given adsorbate and temperature. If the interface is modeled as molecularly smooth, agreement between theory and experiment is poor. If, on the other hand, one assumes that fine-scale asperities are randomly scattered over the electro-polished surfaces good agreement is obtained. The test surfaces will, therefore, be examined by electron microscopy, to get information regarding the asperities, to feed into the theory.

In its present form, the theory enables one to estimate from the test results the heat of adsorption at the interface and the maximum normal stress under which equilibrium adsorption is possible.

The adsorption experiments are being continued, since they appear to be simple enough to be analyzed in terms of basic principles. It is hoped that the understanding of so-called "boundary lubrication" may thus be advanced.

## 2.0 Fundamental Bearing and Seal Research

Personnel: Professor W. D. Syniuta; C. Corrow

Sponsorship: Pratt and Whitney Division of United Aircraft, DSR 70581

Research Report

A study of rolling contact fatigue as produced on a Barwell 4 ball rig was undertaken. Optical and electron microscopy techniques were used to determine the origin of fatigue cracks. The effect of load, of speed, of temperature, of lubricants and of moisture on fatigue life were studied.

At 10% of the life of a specimen, micron size cracks appeared on the stressed surface. With further running more cracks appeared, but those existing did not grow to any extent except for isolated cases. When the lubricant was changed, cracks appeared at the same fraction of total life. Etching of the ball tracks showed that the surface cracks observed were almost always located at the chrome carbide to martensite interface.

Fractography studies of fatigue spalls were undertaken. Cracks leading to spalling began at the surface in three of four cases which were studied.

Cathode polarization of the balls gave a three-fold reduction in life, but anodic polarization had no effect.

3.0 Basic Studies in Grinding

Personnel: Professors N. H. Cook, E. Rabinowicz; S. Malkin

Sponsorship: The Norton Company, DSR 76056

Research Report

Tests are being conducted to determine the factors which influence the mechanism and extent of grinding wheel wear. The wear particle from the grinding wheel are collected, sieved, and weighed. The particle size distribution obtained in this manner is compared to the particle size distribution of the abrasive grain used in manufacturing the grinding wheel. Preliminary results indicate that most of the wear (about 70% by weight) is due to fracture of the grains from the bonding agent in the wheel.

The attritious wear of the grains sliding over the workpiece is also measured using a microscope attached directly to the grinding machine. Harder grinding wheels (grinding wheels containing high percentages of bonding material) exhibit larger wear flat areas. The wear flat areas also appear to be directly related to the grinding forces.

## 4.0 The Mechanism of Polishing

Personnel: Professor E. Rabinowicz; J. D. Vitkauskas

Sponsorship: Sloan Basic Research Fund

### Research Report

Polishing tests have been carried out over a wide range of conditions. It has been found that a necessary condition for polishing is that the load on each abrasive grit is below some characteristic value. This value may be reached by using large grits and a soft backing or small grits and hard backing. Similarly, in the absence of abrasives, liding surfaces become burnished if the load per contact point is low, and roughened if the load per contact is high.

There is an analogy between material removal during sliding and material removal by evaporation from a liquid. Removal on an atomic scale leaves a smooth surface, while removal on a large scale produces a rough surface. The transition from one mechanism to another is governed by surface energy considerations and occurs at a critical value of energy input into the system..

### Theses

J. D. Vitkauskas, "Velocity Effects on the Polishing of Metals," Nav. Eng. Thesis, Department of Mechanical Engineering, June 1967.

### Publications

E. Rabinowicz, Polishing of Metals, to be published in Scientific American.

E. Rabinowicz, Wear Mechanism for Very Lightly Loaded Surfaces, to be published in Proceedings of Conference on Lubrication and Wear, Institution of Mechanical Engineers, London, 1967.

B. G. Rightmire, "Adsorption at a Solid-Solid Interface," to be submitted for publication. Preprints Available from author or from Industrial Liaison Office, MIT.

## VII. SURFACE PROPERTIES AND PROCESSES

### Personnel

Professor R. E. Stickney, Associate Professor, Mechanical Engineering
Dr. T. J. Lee, DSR Staff, Research Laboratory of Electronics
D. L. Fehrs, Research Assistant, Mechanical Engineering
R. J. Weetman, Research Assistant, Mechanical Engineering
S. A. Doret, Research Assistant, Mechanical Engineering
F. W. Eberle, Research Assistant, Mechanical Engineering
S. Yamamoto, Research Assistant, Mechanical Engineering
H. Miller, Graduate Student, Mechanical Engineering
D. S. Shupe, Graduate Student, Mechanical Engineering
F. J. Walker, Jr., Graduate Student, Mechanical Engineering
J. C. Batty, Graduate Student, Mechanical Engineering
H. C. Juvkam-Wold, Graduate Student, Mechanical Engineering
T. Viswanathan, Graduate Student, Mechanical Engineering
L. E. Sprague, Project Technician, Research Laboratory of Electronics
Rose S. Hurvitz, Secretary, Mechanical Engineering

### Personnel who have left during the period

Dr. M. L. Shaw, DSR Staff, Research Laboratory of Electronics
W. Greaves, J. F. Kennedy Fellow, Mechanical Engineering
J. W. Gadzuk, Research Assistant, Mechanical Engineering
E. G. DeNigris, Graduate Student, Mechanical Engineering

### Degrees Granted

J. W. Gadzuk, Ph.D., January 1967
E. G. DeNigris, S.M., September 1967
H. C. Juvkam-Wold, S.M., September 1967
T. Viswanathan, S.M., June 1967

### Sponsorship

Research Laboratory of Electronics supported in part by the Joint Services Electronics program under Contract DA 28-043-AMC-02536(E);

and in part by National Aeronautics and Space Administration, Grant No. NGR-22-009-091, Lewis Research Center, Cleveland, Ohio; and in part by Interlox, Ltd.; and in part by Cabot Solar Energy Fund.

## Research Report

The general purpose of our research program is to study problems relating to the atomic, molecular, and electronic processes occurring at the gas-solid interface. Examples of these problems are: thermionic emission, surface ionization, adsorption, oxidation, catalysis by metals, photoelectric emission, electrode processes in electrical discharges, and the scattering of molecular beams from solid surfaces. At present, we are concentrating on the following problems.

### 1.0 Adsorption of Gases and Vapors on Solid Surfaces

The objective of this study is to contribute to the development of a theory of adsorption of gases or vapors on metallic surfaces. Our major effort is directed toward obtaining experimental data on both the energy and dipole moment of the adsorption bond between the adsorbate and the substrate. The dipole moment is inferred from measurements of the change in work function during adsorption. Thermionic, photoelectric, and contact-potential techniques are used in these studies. A modulated molecular beam system is now being developed for determination of the desorption energy of various adsorbate-substrate systems. To obtain surfaces that are both clean and well-defined, single-crystal specimens are employed together with ultrahigh vacuum techniques. The adsorbates being considered at this time are the alkali metals, halogens, oxygen, nitrogen, and hydrogen.

### 2.0 Catalysis and Oxidation

Using modulated molecular beam and mass spectrometric techniques, we are investigating the catalytic formation of ammonia on iron and the oxidation of tungsten. Our principal objective is to determine the dependence of the rates of these reactions on temperature, pressure, and material properties. Thermodynamic and kinetic analyses of these processes are also being performed.

### 3.0 Scattering of Gas Atoms and Molecules from Solid Surfaces

The collisions of gas atoms and molecules with solid surfaces are being studied by means of modulated molecular beam techniques. The principal goal of the investigation is to determine the energy and momentum transfer associated with gas-solid collisions. We are now developing an experimental apparatus for measuring the scattering patterns for the collision of argon with a single crystal of silicon which is covered to a known degree with an alkali adsorbate.

### 4.0 Electrode Processes in Electrical Discharges

Recently we have become interested in the interaction of an arc or a spark with a metallic electrode, especially for those conditions encountered in electrical discharge machining. Experiments are being conducted to determine the mechanism responsible for the erosion of material from the electrode surfaces.

### Theses

J. W. Gadzuk, "Many-Body Theory of a Rapidly Varying, Inhomogeneous Electron Gas," Ph. D. Thesis, Department of Mechanical Engineering, January 1968.

E. G. DeNigris, "The Heat Transfer Aspects of Electrical Discharge Machining," S. M. Thesis, Department of Mechanical Engineering, September 1967.

H. C. Juvkam-Wold, "An Experimental Investigation of Electrical Discharge Machining Using Reverse Polarity," S. M. Thesis, Department of Mechanical Engineering, September 1967.

T. Viswanathan, "Boiling Heat Transfer Coefficients of Multi Component Mixtures," M. S. Thesis, Department of Mechanical Engineering, June 1967.

### Publications

R. E. Stickney, P. B. Sun, and M. L. Shaw, "Effect of Thermal and Ultraviolet Radiation on Thermionic Emission from Tungsten," J. Appl. Phys. 37, 2391 (1966).

R. E. Stickney, R. F. Keating, S. Yamamoto, and W. J. Hastings, "Angular Distribution of Flow from Orifices and Tubes at High

Knudsen Numbers," J. Vac. Sci. Technol. 4, 10 (1967).

D. L. Fehrs and R. E. Stickney, "Contact-Potential Measurements of the Adsorption of Cs, $O_2$, and $H_2$ on (110) Ta," Surface Sci. 8, 267 (1967).

S. Yamamoto and R. E. Stickney, "Analysis of Lock-In Detection of Modulated Molecular Beams Scattered from Solid Surfaces," J. Chem. Phys. 47 1091 (1967).

M. L. Shaw and R. E. Stickney, "Comment of the Paper 'Photoelectric Ion Emission from Cesiated Surfaces'," Phys. Rev. Letters 18, 824 (1967).

R. E. Stickney, W. Greaves, and D. L. Fehrs, "Experimental Measurements of the Work Functions and Desorption Energies of the Systems O-W, O-Mo, O-Re, O-Ta, and Cs-O-Ta," in Report on 1967 Thermionic Specialists Conference, I. E. E. E., (1967) in press.

R. E. Stickney, "Atomic and Molecular Scattering from Solid Surfaces," in Advances in Atomic and Molecular Physics, Vol. III (D. Bates and I. Estermann, editors), Academic Press, N. Y. (1967) pp. 143-204.

## VIII. CRYOGENIC ENGINEERING LABORATORY

## MECHANICAL ENGINEERING DEPARTMENT

### Personnel

Professor J. L. Smith, Jr., Associate Professor, Mechanical Engineering
Professor J. Gerstmann, Assistant Professor, Mechanical Engineering
Professor E. G. Cravalho, Assistant Professor, Mechanical Engineering
R. P. Cavileer, DSR Staff, Mechanical Engineering
P. M. Andersen, Research Assistant, Mechanical Engineering
F. E. Becker, Research Assistant, Mechanical Engineering
K. R. Diller, Research Assistant, Mechanical Engineering
K. Koenig, Research Assistant, Mechanical Engineering
E. B. Qvale, Research Assistant, Mechanical Engineering
P. Thullen, Hertz Foundation Fellow, Mechanical Engineering
P. A. Rios y Cartaya, Air Reduction Company Fellow, Mechanical Engineering
T. J. Tennison, III, Research Assistant, Mechanical Engineering
K. H. Benner, Machinist, Mechanical Engineering
R. D. Gertsen, Technician, Mechanical Engineering
J. O'Callaghan, Machinist, Mechanical Engineering
W. J. Shea, Mechanic, Mechanical Engineering
Rachel P. Levin, Administrative Assistant, Mechanical Engineering
Susan P. Russell, Secretary, Mechanical Engineering

### Degrees Granted

E. B. Qvale, Ph.D., Mechanical Engineering, January 1967
P. A. Rios y Cartaya, S.M., Mechanical Engineering, January 1967; Mechanical Engineer, June 1967
P. Thullen, S.M., Mechanical Engineering, January 1967

### Sponsorship

Partly self-supporting
Lincoln Laboratory, AF 19(268)-5167, P. O. No. CC 900, DSR 76140

Metal Bellows Corporation (Grant-in-Aid), DSR 70224

## Research Report

The continuing activities in the Laboratory include: investigation of refrigeration cycles of the Stirling type, application of metal-bellows expansion engines and compressors to miniature cryogenic refrigeration systems, the influence of surface material and surface properties on the boiling heat transfer to liquid helium, and forced-convective heat transfer to supercritical helium.

The Laboratory effort on the application of cryogenics to electric power generation and utilization has focused on large synchronous machines with superconducting field windings.

New projects have been initiated on the engineering problems of refrigeration below $1^{o}K$ with $He^3$-$He^4$ mixtures, the thermal radiation properties of solids at cryogenic temperatures, and the propagation of thermal radiation in absorbing media.

The facilities and services of the Cryogenic Engineering Laboratory have continued to be available to and widely utilized by the Institute Community. Approximately 75,000 liters of liquid helium were supplied in the last year.

## Theses

E. B. Qvale, "An Analytical Model of Stirling-type Engines", Ph.D. Thesis, Department of Mechanical Engineering, January 1967.

P. A. Rios y Cartaya, "The Effect of Variable Specific Heat of the Matrix on the Performance of Thermal Regenerators", S.M. Thesis, Department of Mechanical Engineering, February 1967; Mechanical Engineer, June 1967.

P. Thullen, "Model for Thermally Sustained Pressure Oscillations in Liquid Helium", S.M. Thesis, Department of Mechanical Engineering, January 1967.

## Publications

J. W. Colangelo, E. E. Fitzpatrick, S. N. Rea and J. L. Smith, Jr., "An Analysis of the Performing of the Pulse Tube Refrigerator", presented at the 1967 Cryogenic Engineering Conference and for publication in Advances in Cryogenic Engineering.

P. A. Rios y Cartaya and J. L. Smith, Jr., "The Effect of Variable Specific Heat of the Matrix on the Performance of Thermal Regenerators", presented at the 1967 Cryogenic Engineering Conference and for publication in Advances in Cryogenic Engineering.

P. Thullen and J. L. Smith, Jr., "Model for Thermally Sustained Pressure Oscillations Associated with Liquid Helium", presented at the 1967 Cryogenic Engineering Conference and for publication in Advances in Cryogenic Engineering.

E. B. Qvale and J. L. Smith, Jr., "A Mathematical Model for Steady Operation of Stirling-Type Engines", preprint, Paper No. 67-WA/Ener-1, presented at ASME 1967 Winter Annual Meeting, November 12-17, Pittsburgh, Pa. and for publication in Transactions of ASME, Journal of Engineering for Power.

E. G. Cravalho, C. L. Tien, and R. P. Caren, "Effect of Small Spacings on Radiative Transfer Between Two Dielectrics", Journal of Heat Transfer, Transactions of ASME, series C, Vol. 89, pp. 351-358, 1967.

C. L. Tien and E. G. Cravalho, "Thermal Radiation of Solids at Cryogenic Temperatures", presented at the Symposium on Advances in Cryogenic Heat Transfer, American Institute of Chemical Engineers 60th Annual Meeting, New York, November 20 26, 1967. Also to be published in the anthology, Advances in Cryogenic Heat Transfer, 1968.

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# IX. CHEMICAL ENGINEERING OF MATERIALS

## 1.0 Polymeric Materials

### 1.1 Properties of Complex Coacervates of Polyelectrolytes

#### Personnel

Professor A. S. Hoffman, Associate Professor, Chemical Engineering
D. Wu, A. D. Little Fellow, Chemical Engineering
A. Azizoglu, Graduate Student, Chemical Engineering

#### Sponsorship

None at present

#### Research Report

The mechanical properties of complex coacervates of polyanions and polycations are being investigated. The major material variable is the charge density on the individual polyelectrolyte backbones. This is controlled by the ratio of charged to non-charged monomers used to prepare the polyanions or polycations by copolymerization. Swelling and salt sorption data of the coacervates are being obtained in order to extend the theory of complex coacervation to coacervates of varying, controlled charge density. These data enable modelling of the microstructure and thus better interpretation and understanding of the mechanical properties.

## 2.0 Catalysis

### 2.1 Semiconductor Catalysis

#### Personnel

Professor R. F. Baddour, Professor, Chemical Engineering
Professor C. W. Selvidge, Assistant Professor, Chemical Engineering
S. Mitchell, Technician, Chemical Engineering

Sponsorship

Office of Naval Research, Nonr 3963(04), DSR 79423

Research Report

Techniques have been developed to investigate the catalytic and chemical properties of atomically clean elemental semiconductor surfaces. These techniques have been used to obtain data relating catalytic activity to controlled changes in surface stoichiometry and structure. Work is continuing on various systems.

Publications

R. F. Baddour and C. W. Selvidge, "Catalytic and Chemical Properties of Atomically Clean Germanium Surfaces," J. Phys. Chem., 71, 2536 (1967).

2.2 Interphase Electronic Interactions in Polyphase Solid Catalysts

Personnel

Professor R. F. Baddour, Professor, Chemical Engineering
Professor M. C. Deibert, Assistant Professor, Chemical Engineering
R. W. Kline, Graduate Student, Chemical Engineering
E. M. Norin, Graduate Student, Chemical Engineering
S. Mitchell, Technician, Chemical Engineering

Degrees Granted

E. M. Norin, M.S., Chemical Engineering, January 1968

Sponsorship

National Science Foundation GK-78, DSR 75391

Research Report

The thermal stability and adsorptive properties of high surface area, vacuum crushed germanium powder have been determined.

Germanium powders with surface areas on the order of 100 square centimeters per gram suffer about a ten percent loss in area by sintering under vacuum at 300°C for one hour. Neither the freshly crushed or the sintered germanium powder absorbs measureable quantities of carbon monoxide.

The kinetics of cyclopropane hydrogenation on a pure nickel powder catalyst has been studied to reveal those conditions of reaction composition and temperature in which the activity of the catalyst is most stable. It was found that the activity of the nickel catalyst at 65°C remained relatively constant in a reaction stream in which the ratio of cyclopropane to hydrogen pressure is below one-third. The rate of catalyst deactivation increased in proportion to the cyclopropane content of the reactant stream above this amount. The activity of a deactivated catalyst could be essentially completely recovered by treating the nickel powder at 350°C, first under vacuum and then under a hydrogen atmosphere. These results provide essential criteria for the study of the kinetic properties of the germanium supported nickel catalysts used in the study of the promoting effect of interphase electronic interaction.

Theses

E. W. Norin, "The Kinetics of the Deactivation of a Nickel Catalyst During the Hydrogenation of Cyclopropane", S. M. Thesis Chemical Engineering, January 1968.

## 2.3 Heterogeneous Catalysis

Personnel

Professor R. F. Baddour, Professor, Chemical Engineering
Professor M. Modell, Assistant Professor, Chemical Engineering
J. Aleksandrowicz, Graduate Student, Chemical Engineering
J. B. Harkness, Graduate Student, Chemical Engineering
R. A. Swill, Graduate Student, Chemical Engineering
S. Mitchell, Technician, Chemical Engineering

Sponsorship

National Science Foundation GK-1699X, DSR 70558

Research Report

A catalyzed reaction consists of a sequence of elementary reactions. Previous attempts to correlate overall reaction rates have met with little success. On the other hand, specific rate constants of the elementary reactions should be more amenable to correlation. Specific rate constants can be calculated if the mechanism of a reaction is known and in the concentrations of surface intermediates are measured. At the present time, there is no general and direct method of determining the mechanism. The objective of this research program is to develop a method which would be applicalbe to gas-phase, metal-catalyzed reactions. A method has been proposed, which consists in measuring simultaneously the overall reaction rate and the concentrations of surface intermediates as function of temperature and reactant pressures. Infrared spectroscopy is used to measure surface concentrations. Postulated mechanisms can then be tested directly by comparing experimental and theoretical forms of the rate, expressed in terms of surface concentrations.

In an experimental program initiated in 1963, simultaneous infrared and kinetic measurements were made for CO oxidation on silica-supported palladium catalysts. For the CO-Pd system, two types of surface species were indentified by infrared spectroscopy. Palladium-oxygen absorption bands were not observed because the background absorption of the silica support is intense in the region where $Pd\text{-}O_2$ bands are believed to occur. The results indicated clearly the inadequacy of the conventional kinetic approach and the value of simultaneous measruements. However, the experiments were not sufficient to identify unequivocally the reaction mechanism. Two essential pieces of data were lacking: spectroscopic observation of the palladium-oxygen species, and extinction coefficients of the surface species.

A program is in progress for obtaining absolute values of surface concentrations by measuring the relative extinction coefficients of adsorbed species. The method essentially involves relating the increase in total amount of gas adsorbed during sequential dosing of a catalyst with adsorbate to the relative increase in integral absorbance of the infrared bands. When the extinction coefficients have been determined, simultaneous measurements of kinetics and spectra will be made over wide ranges of surface coverage.

A second set of experiments is in progress to develop general techniques for observing infrared absorption bands of all surface species. The conventional infrared method involves transmission spectroscopy in which small particles of metal (50 Å) are supported on finely divided silica or alumina (100 Å). Large regions of the infrared are obscurred by the intense adsorption of these supports. Thus, palladium-oxygen bonds have not been observed because they are believed to occur in the region of the silica continuum. In an effort to surmount the limitations of conventional transmission spectroscopy, reflection spectra of unsupported metals are being observed. An interferometer spectrometer is being used to measure the weak signals which are obtained. It is estimated that fifty to one hundred bounces will be required to obtain quantitative spectra at surfaces coverages down to 1% of a monolayer. The region from 2.5 to 40$\mu$ is being investigated.

## 2.4 Diffusion in Porous Materials

### Personnel

Professor C. N. Satterfield, Professor, Chemical Engineering
W. G. Margetts, Graduate Student, Chemical Engineering

### Personnel who have left during the period

Dr. P. J. Cadle
Dr. H. Iino
Dr. Y. H. Ma
Dr. A. Pelossof

### Degrees Granted

P. J. Cadle, Sc. D., Chemical Engineering, January 1967
H. Iino, Sc. D., Chemical Engineering, January 1967
Y. H. Ma, Sc. D., Chemical Engineering, January 1967
A. Pelossof, Sc. D., Chemical Engineering, June 1967

### Sponsorship

National Aeronautics and Space Administration (Center for Space Research
NsG-496 (part), DSR 76183
National Science Foundation, Grant GK-565, DSR 76019

Research Report

The doctoral thesis of Cadle has clarified many questions concerning our ability to predict the diffusion flux of gases in porous catalysts. Many previous studies reported in the literature have been obtained on porous masses prepared by pressing a powder into a die and the results have been analysed assuming that the porous structure is uniform. However, Cadle's studies with a powdered alumina and earlier studies in our laboratory with a hard chromia-alumina catalyst powder as pellets 3/8-inch or 1-inch in diamter show that the variation of effective diffusivities or pellets pressed from these powders can vary by a factor of as much as 3 or 4 with actual distance through the compact, and the results can be interpreted in terms of the density distribution patterns. Consequently, the results of such studies cannot be used for validation of various proposed models for diffusion through porous catalysts.

Commercial pelleted catalysts, on the other hand, appear to be much more uniform, probably because of the difference in the pressing techniques and the fact that the pellets are usually subjected to a calcination treatment after pressing in which the gas that is evolved helps to modify anisotropies such as skin effects. Studies of the diffusivity characteristics of seventeen different commercially manufactured pelleted catalysts and catalyst supports were measured by a steady-state gaseous counterdiffusion method. The results were analysed in terms of a model in which the pores of various sized were assumed to be in parallel and a tortuosity factor was invoked to account for deficiencies in the assumption that all the pores are oriented in the direction of diffusion and that they are of uniform radius. Except for two materials which apparently had been calcined at very high temperatures, tortuosity factors all fell between 3 and 7. Methods of predicing diffusion at elevated pressures in the presence of simultaneous forced flow were also developed from studies on a group of five commerical porous catalysts. The results could be well correlated in terms of the "dusty gas model" of Evans, Watson, and Mason. Studies of diffusion in the absence of forced flow at elevated pressures were well correlated by the parallel path pore model used for studies at atmospheric pressure.

In the Sc. D. Thesis of Margetts, diffusion studies in mordenite continue with gases chosen for such characteristics as their interaction energy with a solid or their molecular shape.

To date the following gas pairs have been studied in the pressure range of 0.5 to 30 mm Hg at the temperature specified:

| Gas | Temperature |
|---|---|
| Kr | liquid nitrogen |
| $CH_4$ | 25, 65, 110°C. |
| $SF_6$ | solid $CO_2$ |
| $C_4F_{10}$ | 25° C. |
| $C_4H_{10}$ | 25° C. |
| iso $C_4H_{10}$ | 25, 100, 200° C. |
| $C_4H_8$ | 25° C. |

Generally, no available unsteady-state diffusion equation fits the experimental data adequately. In a Fick's law relationship the diffusivity, D, decreases as the amount sorbed increases. For sorption times between approximately 10 and 40 to 60 seconds, an $M_T/M_\infty$ versus $\sqrt{t}$ plot (Crank solution) gives a linear relationship and consequently a constant D. Below 10 seconds, preliminary analyses show that D increases by about one order of magnitude. Above 40 to 60 seconds, D decreases by many orders of magnitude. Various other models are being tested to see if they will provide a more adequate representation of the results.

The two doctoral theses by Y. H. Ma and by A. Pelossof, jointly supervised with Professor T. K. Sherwood, were concerned with mass transfer limitations in a trickle bed reactor. A portion of their investigation was concerned with the problem of diffusion in liquid-filled porous catalysts. Ma's study showed that the analytical method for prediction of the catalyst effectiveness factor applies well to the case in which the catalyst pores are filled with liquid. The liquid-phase hydrogenation of alpha-methylstryrene to cumene on a palladium-alumina catalyst was studied at 70 to 115°C. and atmospheric pressure using catalyst pellets of two sizes and powdered pellets. The effectiveness factors for the pellets, which were found to vary from 0.07 to 0.13, could be brought into agreement with theory by using a reasonable tortuosity value of 3.9. The hydrogenation of alphamethylstryene to cumene was likewise studied in the thesis of Pelossof who studied spherical porous palladium-on-alumina pellets. In his case, the effectiveness factor of the pellets alone at 50°C. was 0.0057 and a relatively high tortuosity factor of 7.5 was ascribed to a skin effect.

## Theses

P. J. Cadle, "Diffusion of Gases in Pelleted Catalysts", Sc. D. Thesis, Department of Chemical Engineering, December 1966.

H. Iino, "Surface Diffusion of Chemisorbed Hydrogen on Nickel", Sc. D. Thesis, Department of Chemical Engineering, November 1966.

Y. H. Ma, "Effectiveness Factor in a Liquid-Filled Porous Catalyst", Sc. D. Thesis, Department of Chemical Engineering, December 1966.

A. A. Pelossof, "Mass Transfer Limitations in a Trickle-Bed Reactor", Sc. D. Thesis, Department of Chemical Engineering, March 1967.

## Publications

J. S. Hartman, G. W. Roberts, and C. N. Satterfield, "Effects of Initial Conditions on the Steady-State Activity of Catalyst Particles", Ind. Eng. Chem. Fundamentals, 6, 80 (1967).

C. N. Satterfield and A. J. Frabetti, Jr., "Diffusion of Hydrocarbons in the Zeolite Mordenite", A. I. Ch. E. Journal, 13, 731 (1967).

C. N. Satterfield and H. Iino, "Surface Diffusion of Chemisorbed Hydrogen on Nickel", Ind. Eng. Chem. Fundamentals, in press.

P. J. Cadle and C. N. Satterfield, "Uniformity of Diffusivity in a Nickel Base Steam-Hydrocarbon Reforming Catalyst", Ind. Eng. Chem. Fundamentals, in press.

C. N. Satterfield and P. J. Cadle, "Diffusion in Commercially Manufactured Pelleted Catalysts", Ind. Eng. Chem., Process Des. and Develop., in press.

P. J. Cadle and C. N. Satterfield, "Anisotropic Diffusivities in Pressed Boehmite Pellets," Ind. Eng. Chem. Fundamentals, in press.

C. N. Satterfield and P. J. Cadle, "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels Above Atmospheric", Ind. Eng. Chem. Fundamentals, in press.

C. N. Satterfield, Y. H. Ma, and T. K. Sherwood, "The Effectiveness Factor in a Liquid-Filled Porous Catalyst", submitted to the Institution of Chemical Engineers (London).

C. N. Satterfield, A. A. Pelossof, and T. K. Sherwood, "Mass Transfer Limitations in a Trickle-Bed Reactor", submitted to A. I. Ch. E. Journal.

H. S. P. Kao and C. N. Satterfield, "Effectiveness Factors for Reversible Reactions", submitted to Ind. Eng. Chem. Fundamentals.

## 2.5 Molecular Sieve (Zeolite) Catalysts

### Personnel

Professor C. N. Satterfield, Professor, Chemical Engineering
Professor W. R. Vieth, Associate Professor, Chemical Engineering
J. R. Katzer, Doctoral Candidate, Chemical Engineering

### Sponsorship

National Science Foundation Grant GK-1707, DSR 70554

### Research Report

The model reaction system chosen for this study is the alkylation of benzene with propylene to form cumene. However, it has been found that the diffusion characteristics of the hydrocarbons in zeolites are highly complicated and recent work has focused on the diffusion characteristics of benzene and cumene in two important zeolites, namely mordenite and Type Y zeolite. In hydrogen mordenite the diffusion rates of benzene and cumene are very slow and the equilibirum is not established over a period of several days at either 25 or 65$^{o}$C. It appears that counterdiffusion cannot occur on this catalyst, although this is required if the interior structure is to be effective in reaction. Counterdiffusion does appear to occur freely in Type Y zeolite. It has been shown by ESR measurements that radical ions are formed when benzene or cumene is adsorbed in H-mordenite and some of the abnormalities of diffusion characteritstics may be attributable to the blockage of pores occurring over periods of hours or days by these radical ions.

## 3.0 Cryogenic Chemistry

### Personnel

Professor R. C. Reid, Professor, Chemical Engineering
J. Merle Ditz, Research Assistant, Chemical Engineering
Ramon Espino, Research Assistant, Chemical Engineering

Sponsorship

National Science Foundation Grant, GK-142, DSR 74614
National Science Foundation Grant, GK-1021, DSR 76384

Research Report

Reactions of atomic hydrogen with solid olefin films have been studied using an electron spin resonance spectrometer to monitor the hydrogen atomic concentration during the course of the reaction. The olefins studied were propylene, 3-methyl butene-1 and methyl acetylene. The effect of film thickness, olefin concentration and temperature were investigated in order to determine the radical mechanism and the influence of diffusion on the reaction. The experimental rates of reaction are in agreement with reaction rates predicted by a diffusion-reaction mathematical model.

The permeation rate of atomic hydrogen through films of solidified, light hydrocarbons ($C_3$ to $C_6$) was studied at 77°K by colorimetric techniques. Smooth films of molybdenum trioxide ($MoO_3$), formed by vacuum deposition, were covered by thin (0.1 to 1.0 micron) films of hydrocarbons. Atomic hydrogen was generated in the gas phase by a microwave discharge. Since hydrogen atoms rapidly reduce $MoO_3$ with a resulting color change, the rate at which atomic hydrogen reached the $MoO_3$ could be determined by continuously monitoring the intensity of monochromatic light reflected from the $MoO_3$ surface. This permeation data as a function of film thickness also indicates the rate at which atomic hydrogen recombines within the hydrocarbon film. Different hydrocarbons were shown to have greatly different permeation rates. These data are very useful in clarifying the mechanism of hydrogen atom-olefin reactions.

## 4.0 Reverse Osmosis Desalination Membranes

Personnel

Professor A. S. Hoffman, Associate Professor, Chemical Engineering
Professor M. Modell, Assistant Professor, Chemical Engineering
T. A. Jadwin, Research Assistant, Chemical Engineering
A. Azizoglu, Research Assistant, Chemical Engineering
R. Leonard, Research Assistant, Chemical Engineering
P. Pan, Research Assistant, Chemical Engineering

M. Sze, Research Assistant, Chemical Engineering

Sponsorship

Office of Saline Water, U. S. Department of the Interior, Grant No. 14-01-0001-1256, DSR 70641

Research Report

New membranes for desalination by reverse osmosis are being prepared by polymerization techniques from a variety of different monomer mixtures. Two "families" of membranes have been developed: (1) hydroxy ethyl methacrylate + methacrylic acid + trimethylol propane trimethacrylate and (2) N-methylol acrylamide + acrylic acid + ethylacrylate (or buryl methacrylate ) + trimethylol propane trimethacrylate.

The membranes are first characterized as to salt and water contents in salt solution. There the direct osmosis of salt is measured and finally reverse osmosis under high pressure is studied as a function of salt content (osmotic pressure) and hydrostatic pressure.

Recent membranes developed are as good as the best membranes currently available (cellulose acetate) and attempts are being made to surface polymerize these monomer mixtures on porous supports. New membrane compositions are also being studied.

5.0 Properties of Clay-Water Systems

Personnel

Professor A. S. Hoffman, Associate Professor, Chemical Engineering
J. Sobel, Research Assistant, Chemical Engineering

Research Report

The phenomenon of dilatancy (reversible shear hardening) has been investigated in aqueous deflocculated kaolinite suspensions. Five different fractions of a whole clay were investigated and the onset of dilatancy was correlated with particle size,shape and concentration. The effect of different dispersants was also investigated. The conclusions which have been reached may be summarized as follows:

1. The phenomenon of dilatancy is a result of the direct particle collision and the buildup of particle clusters. Factors which influence the collision rate and cluster formation control the degree of dilatancy of a suspension.

2. Dilatancy can be expressed quantitatively by the expression:

$$I + C\gamma^N$$

where N is defined as the degree of dilatancy and is determined from the slope of the shear stress shear rate characteristics when plotted on log-log coordinates.

3. Shear induced collisions leading to dilatancy require the flow of interstitial fluid from between colliding particles. The hydraulic resistance to flow controls this movement and hence controls dilatancy. The hydraulic resistance is measured by the hydraulic permeability and is dependent on the size, shape, and size distribution of the particles.

4. Dilatancy increases rapidly with concentration above a critical minimum solids concentration and is a maximum at the closest packing concentration, $\phi_{max}$. The degree of dilatancy is dependent on the "free volume" or proximity to close packing given by $(1-\phi/\phi_{max})$. This close packing density is dependent on the particle characteristics.

5. Dilatancy is a minimum for small particles and increases with particle size.

6. Dilatancy is a minimum for isometric particles and increase when the anisometry of the particles does not give a significant rise in permeability.

7. Dilatancy is a minimum when the size distribution of the particles allow close packing of the sediments, and sediments have low permeabilities.

8. Low Newtonian viscosities are not always indicative of low dilatancy.

9. Dilatancy is at a minimum when the repusive potential between particles is a maximum.

10. Dilatancy is at minimum when the electrostatic double layer "thickness" is a maximum.

## 6.0 Biomaterials

### 6.1 Non-Thrombogenic Materials - Membranes for Blood Dialysis and Oxygenation

#### Personnel

Professor E. W. Merrill, Professor, Chemical Engineering
Professor K. A. Smith, Assistant Professor, Chemical Engineering
Professor E. R. Gilliland, Professor, Chemical Engineering
Dr. P. S. Wong
G. A. Pelletier
Dr. E. W. Salzman, Beth Israel Hospital
Dr. W. Gerald Austen, Massachusetts General Hospital

#### Personnel who have left during the period

R. A. Britton

#### Degrees Granted

R. A. Britton, Ph.D., Chemical Engineering, June 1967

#### Sponsorship

U. S. Public Health Service, Contract PH 43-66-491, DSR 76359
National Institutes of Health, Grant HE-08598, DSR 70552

#### Research Report

Development of non-thrombogenic materials based on heparin bonding via ionic and covalent bonds.

Principal effort has been directed to aminoethyl cellulose prepared by reaction of cellulose with ethylene imine, followed by protonation and ionic adsorption of heparin; the cellulose being variously commercial cellophane, de-esterified cellulose esters, and cuprammonium or xanthate solutions.

Current work includes amination of previously crosslinked poly 1,4 cis-butadiene and poly 1,4 cis isoprene, followed by ionic absorption of heparin, and of grafting of quaternary ammonium groups to silicone rubber, followed by heparinization.

Other studies involve covalent bonding of heparin to cellulose via an isocyanate group.

Theses

R. A. Britton, "Non-Thrombogenic Cellophane," Ph.D. Thesis, Department of Chemical Engineering, June 1967.

Publications

E. W. Merrill, et. al., Trans. Am. Soc. Art. Ins. Organs, 12, 139-150 (1966).

E. W. Salzman, et. al., Surgery 61, 1-10 (1967).

## 6.2 Structure and Properties of Elastin

Personnel

Professor H. P. Meissner, Professor, Chemical Engineering
Professor A. S. Hoffman, Associate Professor, Chemical Engineering
D. Mukherjee, Research Assistant, Chemical Engineering

Sponsorship

The Medical Foundation, DSR 70726

Research Report

The rubber-like behavior of body ligament and aorta blood vessel walls is mainly due to the high content of elastin in these components. The structure of elastin is as yet only poorly known, and we are attempting to elucidate this structure by investigating the swelling and mechanical properties of purified ligament (100% elastin). The approach taken is similar to that used to study synthetic rubbers. We have found that the behavior of elastin is typical of a crosslinked rubber, except that its crosslink density appears to depend strongly upon the particular solvent or aqueous salt mixture used to swell it. These studies are continuing and will also be applied to elastin samples of varying age.

# X. EFFECTS OF RADIATION ON MATERIALS

## 1.0 Effects of Radiation on Organic Coolants for Nuclear Reactors

### Personnel

Professor E. A. Mason, Professor, Nuclear Engineering
Professor D. T. Morgan, Visiting Associate Professor, Nuclear Engineering
W. N. Bley, DSR Staff, Nuclear Engineering
S. T. Brewer, DSR Staff, Nuclear Engineering
M. L. Lee, Research Assistant, Nuclear Engineering
G. Yadigaroglu, Research Assistant, Nuclear Engineering
G. Rigamonti, Research Assistant, Nuclear Engineering
H. Spierling, Research Assistant, Nuclear Engineering
R. C. Sanders, Research Assistant, Nuclear Engineering
C. K. Anderson, Graduate Student, Nuclear Engineering
R. Courteny, Northeastern University Cooperative Student
S. Parkhurst, Northeastern University Cooperative Student
E. Pembroke, Northeastern University Cooperative Student
B. Stone, Northeastern University Cooperative Student
D. Safran, Northeastern University Cooperative Student
A. J. Pierni, Chemical Technician, Nuclear Engineering
J. F. Howard, Chemical Technician, Nuclear Engineering
Susan Kelemen, Secretary, Nuclear Engineering

### Personnel who have left during the period

J. W. Steiner, DSR Staff, Nuclear Engineering
T. H. Timmins, Research Assistant, Nuclear Engineering
J. Donohew, Research Assistant, Nuclear Engineering
J. Asbeck, Graduate Student, Electrical Engineering
R. Farookhi, Graduate Student, Chemical Engineering
R. C. Hewitt, Graduate Student, Chemical Engineering
J. Larson, Chemical Technician, Nuclear Engineering
Carol Schwartz, Secretary, Nuclear Engineering

Degrees Granted

T. H. Timmins, Sc. D., Nuclear Engineering, January 1967
J. Donohew, S.M., Nuclear Engineering, September 1966

Sponsorship

Atomic Energy Commission, Savannah River Operations Office,
Contract No. AT(38-1)-334, DSR 79819

Research Report

Organic fluids with low vapor pressures offer several advantages for use as coolants in nuclear reactors. However, such materials undergo radiation damage and in general have poorer heat transfer properties than water when used as reactor coolants. The primary objectives of this research program are the study of the nature and the rate of degradation of organic liquids suitable for use as nuclear reactor coolants when tested under conditions of reactor pressure and temperature and of the effect of the degradation product on the rate of heat transfer and on the other properties pertinent to the use of organic liquids as reactor coolants. Organic liquids are subjected to radiations at various temperatures while being circulated through an in-reactor loop in the MIT Nuclear Reactor.

Effects of reactor irradiation on meta-rich organic coolants such as Santowax OMP and Santowax WR have been studied extensively by MIT. Recent Canadian high dose rate experiments indicate that pure ortho terphenyl is less stable to mixed reactor radiations above about 330°C than pure meta terphenyl. To study the relative stabilities of the isomers in mixtures, in-pile irradiations of Santowax OM (approximately 2:1 ortho terphenyl to meta-terphenyl by weight), have been undertaken for the purpose of obtaining the following information:

(1) The relative rates of degradation of both ortho and meta terphenyls in the ortho-rich coolant,
(2) The relative distribution of degradation products and,
(3) The effects of radiolysis and pyrolysis

The Santowax OM irradiations have employed conditions similar to those previously used in the irradiations of Santowax WR (approximately 1:5 ortho terphenyl to meta terphenyl by weight); coolant temperatures of

300°C, 371°C, 399°C, and 427°C; terphenyl concentrations range from 60 w/o to 90 w/o in the coolant; and dose rates from 0.03 watts/gm. and 0.07 watts/gm. to the total coolant (approximately 0.8 watts/gm. and 1.8 watts/gm maximum in the core). The runs at 300°C and 371°C were made to measure the radiolysis effects and the runs at 399°C and 427°C were made to measure the combined effects of radiolysis and radio-pyrolysis. The two dose rates were employed to show any dose rate effects.

A direct comparison of the G values of total terphenyl and each isomer for the Santowax OM and Santowax WR will permit the determination of the relative stability of the terphenyl isomers in these two terphenyl mixtures, one ortho-rich and the other meta-rich.

Comparison of the results obtained with Santowax WR and Santowax OM indicate that:

(1) The degradation rates of Santowax OM and Santowax WR under similar conditions of irradiation were not significantly different.

(2) The ortho-rich Santowax OM irradiated in a reactor flux yields higher low and intermediate boiler to high boiler ratios than the meta-rich Santowax WR.

## Thesis

T. H. Timmins, "Effect of Reactor Irradiation on Santowax WR", Ph. D. Thesis, Department of Nuclear Engineering, January 1967.

J. N. Donohew, Jr., "A Model for the Calculations of the Fast Neutron Degradation of Santowax WR", S.M. Thesis, Department of Nuclear Engineering,

## Publications

E. A. Mason, M. L. Lee, W. N. Bley, "Cmmparison of Degradation Rates of Santowax OM and Santowax WR," Trans. Am. Nucl. Soc., 10, No. 2, 480 (1967).

## 2.0 Radiation Acceleration of Viscoelastic Processes in Polymers

### Personnel

Professor E. R. Gilliland, Professor, Chemical Engineering
Professor A. S. Hoffman, Associate Professor, Chemical Engineering
R. Mayer, Research Assistant, Chemical Engineering
A. Goldsmith, Bachelor of Science Candidate, Chemical Engineering
K. Nisancioglu, Undergraduate Student, Chemical Engineering

### Sponsorship

Atomic Energy Commission, purchase order from Lawrence Radiation Laboratories, Livermore, California, under Contract W-7405-ENG-48, DSR 70049, 74678, 70626

### Research Report

The temporary acceleration of creep during high intensity irradiation of polystyrene and polymethylmethacrylate (PMMA) has been investigated and it was concluded that the effect is due to generation and temporary accumulation of gases between the polymer chains. Studies are continuing into this phenomenon for polycarbonate.

### Thesis

A. Goldsmith, "Density Changes in Polycarbonate Due to Radiation Accelerated Creep," S.B. Thesis, Department of Chemical Engineering, June 1967.

### Publications

J. P. Bell, A. S. Michaels, A. S. Hoffman and E. A. Mason, "Temporary Acceleration in Creep of Polystyrene during High Intensity Irradiation," Adv. in Chem., No. 66 (1967).

SECTION E

FRANCIS BITTER NATIONAL MAGNET LABORATORY

## FRANCIS BITTER NATIONAL MAGNET LABORATORY

The Francis Bitter National Magnet Laboratory at MIT pursues a program of research in solid state physics and related areas using intense magnetic fields. The central research facility consists of a ten megawatt dc power supply and a number of water-cooled magnets providing continuous field up to 255 kilogauss. Superconducting magnets with fields to 80 kG and a large variety of pulsed magnets with fields to 750 kG are also in use. The development of magnets to provide even higher fields and to meet special experimental requirements is continuing.

The laboratory's research program is primarily a study of the magnetic, electrical, optical and acoustic properties of matter with the aim of increasing understanding of the electronic band structure, the lattice vibration spectrum, phonon-electron interactions and magnetic interactions in solids. A strong magnetic field represents a perturbing environment which alters the effect of materials on the transmission and reflectance of electromagnetic and acoustic radiation. Experimental techniques now in use include single photon, multiphoton and non-linear magneto-optical reflection and absorption, de Haas-van Alphen effect, magnetic resonance, magneto-resistance, Mössbauer effect and acoustic absorption. The use of intense laser light sources and ultra low temperatures with high magnetic fields provides many new experimental opportunities. Theoretical studies of band structure, magnetism, superconductivity and other topics are carried on in close conjunction with the experimental program. The high field facilities are made available to research groups from other MIT departments and from institutions throughout the world.

Sponsorship

Francis Bitter National Magnet Laboratory
Supported by the Air Force Office of Scientific Research
Contract F44620-67-C-0047

# FRANCIS BITTER NATIONAL MAGNET LABORATORY

## Personnel

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Dr. D. T. Stevenson, Assistant Director

E. W. L. Davis, Assistant Director for Administration

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Prof. J. Zak

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Dr. J. Dimmock (Lincoln Laboratory)

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Prof. A. Javan (MIT Physics Department)
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Dr. R. O' Brien (Weston College)
Dr. K. Tachikawa (National Research Institute for Metals, Tokyo)
Dr. J. Trãff (Technical University of Denmark)
Dr. W. Zawadzki (University of Posnan)*
Prof. G. Zimmerman (Boston University)

Graduate Students

D. Abehouse, Graduate Student, Physics (Boston University)
T. Cronburg, Graduate Assistant, Physics (MIT)
T. Bernstein, Graduate Assistant, Physics (MIT)
A. Brecher, Graduate Student, Physics (MIT)
J. M. Cherlow, Graduate Assistant, Physics (MIT)
D. R. Cohn, Graduate Assistant, Physics (MIT)
M. Greenebaum, Graduate Assistant, Physics (MIT)*
W. Hackett, Graduate Assistant, Physics (MIT)
T. Hart, Graduate Assistant, Physics (MIT)
L. Kaufman, Graduate Student, Physics (Tufts)
M. Maltz, Graduate Assistant, E. E. (MIT)
G. Peabody, Graduate Student, Physics (Harvard)
M. Reine, Graduate Studnet, Physics (MIT)
B. Sacks, Graduate Assistant, E. E. (MIT)*
U. Smith, Graduate Assistant, Physics (MIT)
R. Stimets, Graduate Assistant, Physics (MIT)

* Terminated during 1967
** Deceased 1967
*** Leave of absence 1967

Degrees Granted

William Harold Hacket, Jr. Ph. D. Electrical Engineering, January 1967, "Microwave Surface Dependence Measurements of High $^{-K}$ Type Superconductors in High Magnetic Fields".

Yuki Iwasa, Ph. D. Electrical Engineering, June 1967, "Stability and Spatially Periodic Magnetization of Hard Superconductors".

Michael Greenebaum, Ph. D. Physics, June 1967, "Magnetoplastic Waves in Bismuth-Antimony Alloys at High Magnetic Fields".

Barry H. Sacks, Ph. D. Electrical Engineering, June 1967, "Magnetic Field Effects in Semiconductor Lasers".

R. J. Stein, S. B. Thesis, June 1967, "Development of a Cyanide Laser".

L. H. Holley, S. B. Thesis, June 1967, "The De-Hass-Van Alphen Effect in Zinc."

M. D. Zutcek, S. B. Thesis, June 1967, "Magnetopiezo Transmission for the Indirect Transition in Germanium".

# FRANCIS BITTER NATIONAL MAGNET LABORATORY RESEARCH REPORTS

## 1.0 High Field Magnet Development

Personnel: A. Bergles, Y. Iwasa, H. Kolm, M. Leupold, B. Montgomery, R. Weggel, N. Pierce (MIT consultant)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

With the addition of several magnets during the last year, the laboratory now has 25 water-cooled magnets in operation at fields above 100 kilogauss. The majority of magnets operate at a power level of 5 megawatts and this, coupled with increased demand for the 10 magawatt 225 kilogauss magnet, has further saturated the generator facilities. About 10,000 hours of operating time are accumulated by the magnets each year requiring continuous programs of magnet maintenance and reliability improvement.

Major progress has been made during the year on the first combined superconducting and water cooled magnet also called a hybrid magnet. A water cooled insert of 165 kilogauss will be combined with a 60 kilogauss 14 inch room temperature bore superconducting magnet. This system is intended to reduce the power necessary to generate fields of 225 kilogauss from 10 to 5 megawatts, thus allowing two experiments to be run simultaneously at 225 kilogauss. Suitable composite superconductors have been extensively investigated with regard to the effect on copper resistivity of stress and magnetoresistance, current ansitropy, and critical heat flux. Interaction forces between the two coil systems have been investigated and a suitable cryostat designed. The superconducting coil will be held at 20° K when not actually running, resulting in major savings of helium over a system remaining at 4.2° K. The system is expected to be ready for tests before the end of 1968.

Mechanical design of the 300 kilogauss system is nearly completed. During the course of its design new techniques for optimizing design under seven mechanical constraints have been developed. The large outer coils will be constructed by a new principle of coil design which controls stresses and at the same time results in a particularly simple coil construction. The magnet will initially be powered by the 32 MW two second pulse capacity of the present power supply. In its ultimate version, the 16 MW one minute capacity of the generators, applied to the inner coils, will be combined with superconductors outside, as in the hybrid system discussed above, to produce 300 kilogauss for periods up to one minute.

Several smaller superconducting magnets have been completed during the year. A 1.5 inch $NB_3Sn$ 80 kilogauss coil for Mössbauer spectroscopy is now operated for periods up to one week, with helium added and the persistent current adjusted only once every 24 hours.

## Publications


JP 213 S. Foner, W. G. Fisher, "Large Volume Solid Helix Magnets for Pulsed High Fields", Rev. Sci. Instr., 38, 440 (1967).

MS 297 D. Bruce Montgomery, "The Technology and Application of Superconducting Magnets", in Progress in Radio Science, 1963-1966; Proc. of XVth General Assembly of URSI, Munich, Germany, Sept. 5, 1966, p. 2326.

MS 321 D. B. Montgomery, "High Field Magnets at the National Magnet Laboratory", Proc. Intl. Conf. on High Magnetic Fields, Their Production and Application, Colloques Internationaux du CNRS No. 166, p. 51 (1967).

MS 337 B. Lax, "Physics with High Magnetic Fields", Proc. Intl. Conf. on High Magnetic Fields, Their Production and Application, Colloques Internationaux du CNRS No. 166, P. 61 (1967).

TR11 R. F. Lupina, A. E. Bergles, "Heat Transfer and Pressure Drop in Tape Generated Swirl Flow", Rep. 70281-47 F44620-67-C-0047.

MS 356 K. J. Button, "Practical Uses of Superconducting Magnets in Electromagnetic Systems and Devices," Progress in Radio Sciences, 1963-1966; Proc. of XVth General Assembly of URSI, Munich, Sept. 5, 1966. p. 2350.

MS 322 F. Bitter, "The Production of Megagauss Fields and High Pressures by Capacitor Discharge," Intl. Conf. on High Magnetic Fields - Their Production and Application, Greneble, France, Colloques Internationaux du CNRS, No. 166, (1967).

MS 462 E. Saur, H. Wizgall, "Properties of High Field Superconductors in Magnetic Fields up to 230 kOe." Conf. on High Magnetic Fields, Colloques Internationaux du CNRS Nol 166, p. 223 (1967).

## 2.0 Multiphoton Interband Absorption in Semiconductors

Personnel: B. Lax, R. W. Bierig, M. H. Weiler, J. Halpern, N. Blum

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The original results on small gap semiconductors using a Q-switched carbon dioxide laser have been refined. More definitive identification of individual transitions between Landau levels in a magnetic field has been achieved and extensive theoretical work has been initiated which helps to interpret the quantum processes involved. An additional program has been started to study large gap semiconductors with the use of a neodymium-doped yttrium aluminum garnet laser working in conjunction with a conventional, tunable source of photons from a monochrometer. The first large gap semiconductor chosen to be studied is zinc sulfide.

### Publications

JP 170 B. Lax, J. G. Mavroides, "Interband Magneto-optical Effects," Chapter 8 in Physics of III-V Compounds - Semiconductors and Semimetals, Vol. III, Ed. by Beer and Willardson (Academic Press, N. Y., (1967).

## 3.0 Magneto-Optical Studies in Semiconductors

Personnel: C. R. Pidgeon, R. L. Aggarwal, J. Halpern, B. Lax

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The detailed electronic energy band parameters of small gap semiconductors are being determined experimentally by means of the magneto-electro reflectance technique at low temperatures. The experimental data on indium antimonide and indium arsenide has been correlated with a detailed theoretical analysis generated by our computer program for these materials. The experimental observation of higher band Landau transitions allows this treatment to be the most complete one ever carried out on the band structure of semiconductors. The program has been extended to include mercury telluride. The newer modulation method, magneto-piezo-optical reflection has been made to operate in transmission as well and the study of both germanium and silicon has been completed. The conventional magneto-absorption studies of the excitons in cuprous oxide and the complex bands in gallium selenide have been completed.

## Publications


JP 244 B. Lax, J. G. Mavroides, "interband Magneto-optical Studies of Semi-conductors and Semimetals," Appl. Optics 6, 647 (April 1967).

THXXV M. D. Zuteck, "Magnetopiezo Transmission for the Indirect Transition in Germanium," B. S. Thesis, May 1967.

JP 215 C. R. Pidgeon, D. L. Mitchell, R. N. Brown, "Interband Magneto-absorption in InAs and InSb," Phys. Rev., 154, 737 (1967).

JP 235 Q. H. F. Vrehen, W. Zawadzki, M. Reine, "Shift of Landau Levels in the Valance Band of Germanium in Crossed Electric and Magnetic Fields", Phys. Rev. 158, 702 (1967).

JP 248 J. L. Brebner, J. Halpern, E. Mooser, "Feinstrucktur des Excitmen-Spektrums in GaSe", Helvetica Physica Acta 40, 382 (1967).

JP 249 J. L. Brebner, J. Halpern, E. Mooser, "Magneto-optical Absorption in GaSe," Helvetica Physica Acta 40, 385 (1967).

JP 256 C. R. Pidgeon, S. H. Groves, J. Feinleib, "Electroreflectance Study of Interband Magneto-optical Transitions in InAs and InSb at 1.5° K," Solid State Comm. 5, 677 (1967).

JP 257 J. Halpern, B. Zakharchenya, "Energy Band Structure of $Cu_2O$ in the Vicinity of the Fundamental Edge from Magneto-oscillatory Absorption Measurements", Solid State Comm. 5, 633 (1967).

JP 258 R. L. Aggarwal, M. D. Zuteck, B. Lax, "Nonparabolicity of the $L_1$ Conduction Band in Germanium from Magneto-Piezo-transmission Experiments", Phys. Rev. Letters 19, 236 (1967); erratum 19, 411 (1967).

JP 277 S. H. Groves, R. N. Brown, C. R. Pidgeon, "Interband Magneto-reflection and Band Structure in HgTe", Phys. Rev. 161, 779 (1967).

JP 254 M. Reine, Q. H. Vrehen, B. Lax, "Photon Assisted Magneto tunneling in Germanium in Parallel and Crossed Electric and Magnetic Fields," Phys. Rev. 163, 726 (1967).

JP 255 M. H. Weiler, W. Zawadzki, B. Lax, "Theory of Tunneling and Photon-Assisted Tunneling in Semiconductors in Crossed and Parallel Electric and Magnetic Fields", Phys. Rev. 163, 733 (1967).

## 4.0 Nonlinear Optical Effects in Semiconductor Plasmas

Personnel: B. Lax, M. H. Weiler, R. W. Bierig, K. J. Button, T. L. Cronburg

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The nonparabolic conduction band of some semiconductors permit the observation of nonlinear effects such as frequency multiplicatin, frequency mixing and parametric amplification. Enhancement of these effects in the presence of a high magnetic field has been predicted theoretically. Some of these effects have been observed in the mixing of the two frequencies emitted from the carbon dioxide laser. The high-power, pulsed cyanide laser is being used in an attempt to observe the generation of the third harmonic which has been predicted.

### Publications

THXXII R. J. Stein, "Development of Cyanide Laser," S. B. Thesis, June 1967.

JP 228 B. Lax, W. Zawadzki, M. H. Weiler, "Nonlinear Magneto-Optics of Electrons and Holes in Semiconductors and Semimetals", Phys. Rev. Letters 18, 462 (1967).

## 5.0 Magneto-Plasmon-Phonon Interaction in Semiconductors

Personnel: B. Lax, K. J. Button, T. R. Hart, R. W. Stimets, M. B. Reine, J. Cherlow

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Two different experiments are in progress. The first employs Fourier transform spectroscopy in the wavelength range near the restrahlen bands to study the plasmon-phonon interaction in n-type semiconductors where the plasma frequency is influenced both by the dopin level of the semiconductor and by the applied magnetic field intensity.

The second experiment employs magneto-Raman scattering to study the plasma-shifted Stokes line and its splitting in the presence of a magnetic field.

## 6.0 Submillimeter Cyclotron Resonance

Personnel: K. J. Button, C. C. Bradley, Aviva Brecher, Tsur Bernstein, D. R. Cohn

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The quantum effects in cyclotron resonance of holes in p-type germanium is being studied experimentally to provide the first quantitative correlation with the theoretical predictions of the phenomenon. A continuous wave cyanide laser has been developed for the purpose of collecting the experimental data.

## 7.0 Magneto-Thomson Scattering in Semiconductors

Personnel: B. Lax, T. R. Hart, K. J. Button

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The cross section for the scattering of photons from the electron plasma of a semiconductor in a high magnetic field is greatly enhanced as the magnetic field is increased to approach the cyclotron resonance frequency. The theory of this phenomenon has been evaluated and an experiment has been performed using the carbon dioxide laser. The experimental result confirms the theoretical prediction.

## 8.0 Theory of Semiconductor Lasers in a Magnetic Field

Personnel: B. Lax and B. Sacks

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Computations have been carried out to determine the laser threshold current as a function of temperature for the gallium arsenide laser operating in high magnetic fields. The computer program is capable of providing threshold current data for other semiconductor laser materials as a function of temperature and field intensity.

current data for other semiconductor laser materials as a function of temperature and field intensity.

Publication

THXXVI B.H. Sacks, "Magnetic Feild Effects in Semiconductor Lasers," Ph. D. Thesis, May 1967.

## 9.0 Crystal Growth

Personnel: K. J. Button and M. C. Lavine

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

Singl crystals of rare earth metals are being grown by the vapor deposition method. Semiconductor single crystals, both binary and ternary, are also being grown. In particular, lead-tin selenide has been grown having a composition which adjusts the semiconductor energy gap to that of the photon energy of the carbon dioxide laser.

Publications

MS 296 M. Schieber, "Growth of Samarium, Europium, Thulium and Ytterbium Metals by Vapor Deposition," Intl. Conf. on Crystal Growth, Boston, Mass., June 20, 1966, in Crystal Growth (Suppl. to J. Phys. Chem. Solids) ed. by H. S. Peiser, Pergamon Press, New York, 1967 p. 271.

JP 218 M. M. Schieber, "Crystallization of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ on a Seed in Magnetic Fields up to 140 kOe," Solid State Comm. 5, 353 (1967).

JP 219 M. M. Schieber, "Fluorine-free Flux for Growth of Rare Earth Garnets", Krystal und Technik, March 1967.

JP 231 M. Schieber, "The Effects of High Magnetic Fields on the Isathermal Dissolution and Growth Rates of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ Seed Crystals", J. Crys. Growth, 1 131,(1967).

## 10.0 Experimental Verification of the Fermi-Dirac Distribution of Electrons in Gallium

Personnel: Y. Shapira and L. J. Neuringer

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Much of the theory of the electronic properties of metals hinges on the assumption that the electron distribution function F(E), is equal to the Fermi-Dirac function, f(E). In general, it is not possible to test this assumption directly because of the complicated nature of the relation between F(E) and experimentally observed quantities. An exception is the lineshape of the giant quantum oscillations (GQO) in the ultrasonic absorption which is simply related to F(E). Thus these measurements can be directly applied to a detailed examination of f(E). Using the lineshape of the GQO in gallium at $\sim$ 1.5°K, the function F(E) was deduced and was found to be in good overall agreement with f(E). Measurements in the range of 150 kG are essential in order to resolve the spin-split GQO so that lineshape analysis could be made as a function of temperature and field. To our knowledge this is the first direct experimental verification of the Fermi-Dirac distribution.

### Publication

JP 252 Y. Shapira, L. J. Neuringer, "Experimental Verification of the Fermi-Dirac Distribution of Electrons in Gallium," Phys. Rev. Letters 18, 1133 (June 1967).

## 11.0 Ultrasonic Attenuation in Solids at High Magnetic Fields

Personnel: Y. Shapira and L. J. Neuringer

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Because ultrasonic waves allow introduction of electromagnetic fields into the bulk of metals they are very useful for the studies of the bulk properties of metals, semimetals and semiconductors. Such experiments have been extended to studies of the quantum oscillations of the sound velocity in single crystal gallium at high magnetic fields. Large amplitude quantum oscillations of the ultrasonic velocity, $|\Delta v/v_0| \sim 10^{-3}$, were measured in single crystal gallium at 1.6° K < T < 4.2° K. Observations of the longitudinal sound waves with propagation parallel to the applied field and to the b-crystallographic axes have been made. The results have been compared to three different theories with the most satisfactory account of the experimental observations of the amplitude of the velocity oscillations being given by the Blank-Kaner theory.

Ultrasonic attenuation measurements have been pursued in single crystal uniaxial antiferrimagnets in order to examine the spin-flop transition at high field. Studies below $T_N$ in $(Cr_2O_3)_{0.94} \cdot (Al_2O_3)_{0.06}$, .., at 4.2° K and 77° K, and in $MnF_2$ at 4.2° K in fiels up to 150 kG have been completed. A large variation in attenuation is observed at the spin-flop transition. Measurements from 8-220 MHz for shear and longitudinal waves as a function of crystallographic orientation show several aspects not yet completely explained by existing theories.

## Publications

JP 241 O. Beckman, E. Hanamura, L. J. Neuringer, "Quantum Limit Galvanomagnetic Phenomena in N-InSb," Phys. Rev. Letters 18, 773 (May 1967).

JP 211 Y. Shapira and L. J. Neuringer, "Magnetoacoustic Attenuation in High-Field Superconductors," Phys. Rev. 154, 375 (1967).

JP 239 Y. Shapira, "Absorption Peak for Ultrasonic Waves Near the Spin-Flop Transition of Uniaxial Antiferromagnets," Phys. Letters 24A, 361 (1967).

## 12.0 Resonance Studies at 35 GHz

### 12.1 Cyclotron and Spin Resonance in Graphite

Personnel: H. C. Praddaude, R. O' Brien

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

Cyclotron resonance studies in single crystal and pyrolytic graphite have been completed with high resolution at 35 GHz. A theoretical analysis of the line-shape is now in progress.

Conduction electron spin resonance in graphite has been continued with high resolution at 35 GHz at 4.2° K. The g-shift and anisotrophy have been examined at low temperatures and apparently more than one conduction electron spin resonance line is present. Although the presence of strong Alfven waves and cyclotron resonance indicates high purity in the materials used, and the lines are much broader than those observed for impurities in graphite, further experiments with materials from other sources are in progress in order to study these resonances in greater detail.

## 12.2 Ferromagnetic Resonance in Dilute Alloys

Personnel: H. C. Praddaude and R. O'Brien

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Several metals are currently being examined at the Francis Bitter National Magnet Laboratory which have large exchange enhancements. One such metal, Pd, develops very large localized moments when small amounts of Fe are introduced into the matrix. Although studies of ferromagnetic resonance have been performed at high concentrations of Fe and Pd, very little has been explored in the lower concentration range (less than a few percent Fe in Pd). In order to examine the interaction between the localized Fe moment the high susceptibility Pd matrix we have pursued ferromagnetic resonance in dilute alloys of Fe in Pd down to 100 ppm iron. The g-value, linewidth and linesnape of the observed resonances are strongly concentration and temperature-dependent.

## 12.3 Conduction Electron Spin Resonance in Metals with Localized Moments

Personnel: H. C. Praddaude, R. O'Brien

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The properties of metals with localized moments are of considerable current interest. These include materials which have resistance minima (attributed to the Kondo effect) such as dilute Fe in Cu. High sensitivity reflection cavity techniques at 35 GHz are being used to study the effect of the localized impurity on the conduction electron spin resonance of the matrix. The interaction of the localized moment with the conduction electron may result in a broadening of the electron spin resonance line and/ or a shift in the g-value. By examining this interaction as a function of temperature the effect of the localized moment on the conduction electrons can be observed both above and below the temperature at which the bound state occurs. One of the problems associated with such studies is that the amount of impurity involved is extremely small. By applying ultraclean techniques these studies can be performed for very dilute Fe in Cu and related alloys.

## Publications

JP 224 H. C. Praddaude, "Generalized Transformation to a Rotating Coordinate System in Quantum Mechanics," Phys. Rev. 157, 291 (10 May 1967).

JP 264 R. F. O' Brien, S. Foner, "Cyclotron Resonance in Single Crystal Graphite at 72 GHz" Phys. Letters 25a, 210 (1967).

## 13.0 Magnetic Moment Measurements in Rare Earth Metal Single Crystals

Personnel: E. McNiff, R. Doclo, I. DeGrave, M. Schieber, S. Foner, J. Rhyne (NOL)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

## Research Report

Magnetic moment measurements have been completed in a number of heavy and light rare earth single crystals. The heavy rare earths, Gd, Tb, Ho, Er, and Dy have been examined in fields up to 150 kG along principal axes. Magnetic phase transitions have been observed up to 150 kG and above 4.2° K. Unusual and very large deformations have been observed in both Tb and Dy along the c-axis (hard magnetic axis). A resultant plastic deformation permanently alters the crystallographic as well as magnetic properties of these crystals once they are exposed to fields of the order of 60 kG or more so that such measurements are not useful in evaluating the very high anisotropy. A number of new magnetic transitions, and often incomplete saturation was observed in all materials except Gd.

Magnetic studies in Eu, Sm, Yb, Tm single crystals have also been completed at various fields and temperatures. Almost complete saturation has been observed for thulium along the [10$\bar{1}$0] axis and a linear variation of magnetic moment with field is observed in Eu single crystal. The single crystals were grown at this Laboratory. The magnetic properties of the various rare earths are quite distinct from each other and extremely varied. The magnetic phase transitions will be examined as a function of temperature and field.

Publications

MS 358 S. Foner, E. J. McNiff, "Magnetic Moment Measurements in Single Crystal Dy, Ho, Er, and Gd in DC Fields up to 150 kG," 12th Annual Conf. on Magnetism and Magnetic Materials, Washington, D. C., Nov. 1966; J. Appl. Physics 38, 1377 (March 1967).

MS 379 S. Foner, "Special Magnetic Measurement Techniques," 12th Annual Conf. on Magnetism and Magnetic Materials, Washington, D. C. Nov. 1966; J. Appl. Phys. 38, 1510 (March 1967).

JP 263 S. Foner, M. Schieber, E. J. McNiff, Jr., "Approach to Magnetic Saturation in Single Crystal Thulium at 4.2° K and 140 kG", Phys. Letters 25a, 321 (1967).

## 14.0 The Localized Moments in Dilute Alloys

Personnel: D. Kim, B. Schwartz, E. McNiff, R. Doclo, S. Foner, J. Wernick (Bell Telephone Labs, J. Budnick (Fordham), H. Praddaude, I. DeGrave

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

The exchange enhancement for localized Fe moments in Pd-Fe alloys has been examined with low and high field magnetic moment measurements as a function of temperature and field. The high field susceptibility permits an examination of the matrix susceptibility after the localized moments induced by the magnetic impurities are saturated. The localized moment as a function of concentration has been examined in detail from very dilute (a few ppm Fe in Pd to pure Fe). An interesting by-product of these studies is the observation that most early studies in Pd are in error at low temperature because of the very strong influence of parts per million of Fe in the Pd which results in a large effective moment per Fe atom. Similar effects are seen in Pt.

A second are of direct interest for localized moment studies involves the spin-compensated state (Kondo effect) of dilute alloys. Here an extremely high magnetic field is required in order to suppress the effect. Studies in the Fe-Rh system have been completed up to 150 kG as a function of temperature and field. Indications of a spin-compensated state are observed. Experiments on related systems such as Fe in Cu are also in progress. These results are also to be compared with concurrent Mössbauer studies at high magnetic fields.

## 15.0 High Field Studies of Itinerant Ferromagnets

Personnel: Blum, Frankel, Freeman, Praddaude, McNiff, Foner, Sadagopan (formerly of MIT Metallurgy Dept., now at Avco), Doclo

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

High field magnetic moment measurements have been continued on a number of ferromagnetic metals which show apparent itinerant ferromagnetism. The high field studies on single crystal Fe and Ni have been completed as a function of temperature and field and detailed analysis of the experimental results has also been completed. One of the major problems of previous measurements in moderately high fields has largely been that of systematic errors which are largely removed in the current series of investigations.

A detailed study of polycrystalline and single crystal $ZrZn_2$ has been completed in order to clarify the origin of the ferromagnetism in this compound. It is found that the low field moment is very sensitive to methods of sample preparation and magnetic impurities whereas in high fields, the susceptibility appears to be independent of these effects. More detailed experiments are currently in progress in order to determine whether or not pure $ZrZn_2$ is in fact ferromagnetic at all. This work is also closely related to the studies on $Sc_3In$ which is also thought to be an itinerant ferromagnet. One of the major problems is that extremely high purity is required in order to clearly determine whether or not the ferromagnetism is due to localized moments. Attempts to produce ultrapure $ZrZn_2$ are in progress in order to clarify this situation.

Publication

JP 275 S. Foner, E. J. McNiff, V. Sadagopan, "Magnetic Moment of $ZrZn_2$ up to 150 kG: Is "Pure" $ZrZn_2$ Ferromagnetic?" Phys. Rev. Letters 19, 1233 (1967).

16.0 Exchange Enhancement in Metals and Alloys

Personnel: E. McNiff, R. Doclo, S. Foner

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

A number of the current theories of critical spin fluctuations in metals have been evaluated based on high field magnetic susceptibility measurements in selected materials which apparently have very large exchange enhancement. Studies in pure Pd show that the limits on exchange enhancement are far below those previously suggested by Berk and Schrieffer and others. Present estimates are in the range of eight or less for the exchange enhancement in Pd based on high field magnetic measurements which show that the susceptibility is constant within experimental error up to 150 kG at 4.2°K. Experiments have been in progress in the Pd-Rh alloy series in order to obtain a more definitive limit on exchange enhancement. Preliminary results indicate a comparably low value. Studies of exchange enhancement in alloys on the verge of becoming ferromagnetic are also being made. Systems of current interest are Ni-Rh and Ni-Pd alloys. Both of these are being investigated with high field susceptibility measurements as a function of temperature.

Publication

JP 281 S. Foner, E. J. McNiff, "Magnetic Moment of Pd to 150 kG: Limits of Exchange Engancement in Pd, "Phys. Rev. Letters 19 1438 (1967).

## 17.0 RF Loss and Magnetic Moment Measurements in High Field Superconductors

Personnel: E. McNiff, S. Foner, T. Geballe (Bell Telephone Labs), B. Matthias (Bell Telephone Labs and Univ. of Cal., LaJolla, Cal.)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Measurements of rf loss in a small sample of NbGeAl (a new ~ 20.3° K superconductor) versus temperature show that this material has a critical field of about 150 kG near 16° K. Magnetic moment measurements to 150 kG showed a reversible magnetic moment at 4.2° K and high fields. Preliminary measurements to 213 kG at 4.2° K show that this material is still superconducting. Evidence for the onset of the peak effect near the highest field suggests that the critical field is not far above 213 kG. In order to examine this superconductor in more detail near 4.2° K long-pulse pulsed field experiments are in progress.

Studies of rf loss and magnetic moment in selected, highly reversible, high field superconductors are also being extended to $He^3$ temperatures in search of expected first order magnetic phase transitions.

## 18.0 Magnetoplasma Wave Propagation in High Magnetic Fields in the Bismuth-Antimony Alloy System

Personnel: M. Greenebaum, B. Lax, S. Foner

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The propagation of Alfven and helicon waves in $Bi_{1-x}Sb_x$ alloys at 4.2° K has been measured with 35 and 17 GHz radiation in dc fields to 150 kG. The samples were obtained through the courtesy of Dr. W. M. Yim of RCA Laboratories. Propagation is largely Alfven-wave-like for x = 0.01, with strong quantum modification in both damping and dispersion. For x=0.15, helicons are observed, with Shubnikov-deHaas modulation of the transmission envelope. For x = 0.12, the helicon transmission is strongly affected by the "static" dielectric constant, 100 $\varepsilon_0$ in Bi. In the remaining alloys investigated, x = 0.03, 0.05, 0.08, the spectra are complex, being Alfven-wave-like with a helicon admixture, owing to slight deviations from strict charge carrier compensation. Parameters obtained agree with effective mass and carrier concentration estimates obtained by other techniques. Effects of noncompensation, impure polarization and crystal anisotropy have been studied.

Publications

THXXIV M. Greenebaum, "Magnetoplasma Waves in Bismuth - Antimony Alloys at High Magnetic Fields," Ph. D. Thesis, May 1967.

JP 262 J. K. Furdyna, "Helicons, Magnetoplasma Edge and Faraday Rotation in Solid State Plasmas at Microwave Frequencies," Applied Optics 6, 675 (1967).

## 19.0 Polaron Effective Masses from Cyclotron Resonance

Personnel: J. Hodby, R. Borders, F. Brown (University of Illinois), S. Foner

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report:

Cyclotron resonance has been examined in a series of alkali halides at 140 GHz at 4.2° K and with high dc fields. The polaron effective masses, determined from these measurements, are AgBr (0.33 ± 0.33) $m_e$, AgCl(0.51 ± 0.04)$m_e$, KCl (1.25±0.12)$m_e$, KBr (0.93 ± 0.05)$m_e$, KI(0.67 ± 0.05)$m_e$, RbCl(1.38 ± 0.10)$m_e$, TlCl(0.53 ± 0.05) $m_e$ and (2.72 ± 0.10)$m_e$ where $m_e$ is the free electron mass. This study is part of an extensive program on the alkali halides being pursued at the University of Illinois.

Publication

JP 274 J. W. Hodby, J. A. Borders, F. C. Brown, S. Foner, "Cyclotron Resonance of the Polaron in KCl, KBi, KI, RbCl, AgCl, AgBi, and TiCl," Phys. Rev. Letters 19, 952 (1967).

## 20.0 High Field Superconductivity - Peak Effect

Personnel: E. Maxwell, B. B. Schwartz, K. Hechler

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The peak effect in superconducting niobium nitride has been studied in some detail. This phenomenon is the appearance of a pronounced maximum in the critical current at a field somewhat below the upper critical field. Our investigations have been aimed at understanding the dynamics of flux motion in the superconductor in the neighborhood of the peak region and the underlying mechanism responsible for the peak. We find that the flux movement can be conveniently described in terms of the motion of vacancies in the flux lattice. Our data on niobium nitride suggest that the mechanism responsible for the peak effect is the strong repulsive interactions between adjacent flux bundles.

### Publications

JP 238 E. Lerner, J. G. Daunt, and E. Maxwell, "Magnetic Properties of Superconducting Mo Re Alloys," Phys. Rev. 153, 487 (1967).

JP 246 W. H. Hackett, Jr., E. Maxwell, Y. B. Kim, "Microwave Flux-Flow Dissipation in Paramagnetically-limited Ti-V Alloys," Physics Letters 24a, 663 (June 1967).

JP 259 E. Maxwell, B. B. Schwartz, H. Wizgall, "Flux-hile Motion and the Peak Effect in Superconductivity", Phys. Letters 25a, 139 (1967).

JP 268 K. Hechler, E. Saur, H. Wizgall, "Critical Data of Niobium Nitride in Transverse Magnetic Fields," Z. fur Physik 205, 400 (1967).

THXVII W. H. Hackett, Jr., "Microwave Surface Dependance Measurements of High-K Type II Superconductors at High Magnetic Fields", Ph. D. Thesis, January, 1967.

## 21.0 Adiabatic Demagnetization

Personnel: E. Maxwell, G. Zimmerman, Boston University; D. Abeshouse, Boston University; D. Kelland, R. Frankel

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

We have been studying the properties of cerium magnesium nitrate (CMN) at temperatures down to the order of a millidegree by the technique of adiabatic demagnetization. In a direct one-shot process using fields up to 96 kG we demagnetize to an effective magnetic temperature, $T^*$, of about 2.4 millidegrees (absolute temperature, T< 2 millidegrees). We have observed the susceptibility maximum in CMN and have been using calorimetric techniques to determine the T-T* relation and the specific heat in the region of the maximum. Measurements are being made both on single single crystal spheres and on polycrystalline powders of both spherical and cylindrical shape. The polycrystalline configurations have been used extensively as thermometers by workers in the millidegree region in spite of the fact that no reliable independently determined temperature scale has ever been established for them. We anticipate that our measurements will lead to such a scale.

In another series of experiments adiabatic demagnetization techniques are being used to cool materials down to temperatures of some tens of millidegrees for investigation of the Kondo effect in dilute alloys and superconductivity phenomena at very low temperatures.

## 22.0 Hall Mobility of Ions in Liquid He II Below 1°K

Personnel: F. Dupre, University of Rome; C. E. Chase

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Ions have proved to be a useful probe for studying the properties of liquid helium, and have yielded much information about its microscopic behavior in recent years. The character of the ions themselves is an interesting and still not completely understood problem. Of even greater interest is the nature of their interaction with superfluid helium, which involves collisions with the elementary excitations of the fluid (phons and rotons) and, under appropriate conditions, the creation of quantized vortex rings. In the present experiment, these interactions are studied by observing the deflection of a collimated beam of ions in a strong magnetic field.

The mobility of ions measured by magnetic deflection (Hall mobility) and by time-of-flight techniques need not necessarily be the same. Since the ratio of these mobilities depends on the scattering mechanism involved, measurement of this ratio can yield much useful information. An additional point of interest is that with increasing ion velocity, the time-of-flight mobility decreases in a series of discrete steps whose origin is not understood, and eventually falls sharply as the ion generates a quantized vortex ring. Similar effects in the Hall mobility have not as yet been observed.

We are accordingly measuring the Hall mobility of $He^+$ ions in liquid He II near 0.8° K in order to carry out a comparison with known time-of-flight data. Because a number of experimental problems have been encountered, only preliminary measurements have so far been made. Modifications are under way to remove these difficulties and should lead to reliable results in the near future.

## 23.0 Dielectric Constant, Density, and Equation of State of $^3He$ Near the Critical Point

Personnel: G. O. Zimmerman, Boston University; C. E. Chase

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The problem of critical points has aroused great theoretical and experimental interest recently, and many calssical notions about this region have been proved to be wrong. Although considerable theoretical progress is now being made toward understanding the peculiarly intractable problems which arise, improved experimental data are urgently needed to test new concepts as they are developed. Since there is a close analogy between magnetic critical phenomena (Curie and Neel points) and those observed in fluids, it is to some extent a matter of convenience which one is studied; it turns out that the liquid-vapor phase equilibrium in $^3He$ and $^4He$ is particularly well adapted for the precise measurement of many critical parameters. In addition, $^3He$ until recently appeared to show pronounced deviations from the law of corresponding states in its critical indices, presumably a manifestation of quantum effects. Our current measurements show these deviations to be absent, or at least much smaller than was previously indicated. The experimental technique involves the measurement of the dielectric constant of $^3$He held between the plates of a parallel plate capacitor as a function of temperature and pressure. Our value of $T_c$, the critical temperature, is about 15 millidegrees lower than the previously accepted value, and is believed to be substantially more accurate. The parameters of the coexistence curve and of the equation for the critical isotherm have been accurately determined.

Publications

JP 232 N. M. Whitney, C. E. Chase, "Ultrasonic Velocity and Dispersion in Liquid Helium II", Phys. Rev. 158, 200 (June 5, 1967).

JP 260 G. O. Zimmerman, C. E. Chase, "Orthobaric Density of $^3$He in the Critical Region", Phys. Rev. Letters 19, 151 (1967).

24.0 Oscillating Temperature Technique

Personnel: R. Oder, E. Maxwell

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

We are using temperature and field modulation techniques to obtain direct measurements of the temperature derivative of the magnetic moment, $\frac{\partial \mu}{\partial T}$, and the magnetic field derivative of the thermoelectric power, $\frac{\partial \tau}{\partial H}$, in lightly doped semiconductors where we are searching for direct unambiguous evidence for the presence (or absence) of localized magnetic moments in these materials. Utilizing the temperature modulation technique we have isolated a paramagnetic component of $\frac{\partial \mu}{\partial T}$ measured at 1.5° K for an n-InSb sample doped to $10^{18}$ electrons/cc which is well fitted by a Brillouin function.

We are also employing the temperature modulation technique in a study of the structure of the magnetic phase transition in a series of Pd-Fe alloys. From precise measurements of $\frac{\partial \mu}{\partial T}$ we can obtain the Curie temperature, the field broadening of the transition, the spin-wave contribution to the magnetization at low temperatures, and the paramagnetism induced by the iron impurities in the high temperature region. Our measurements on the alloys of nominal concentration 0.1 and 0.25 wt % Fe in Pd have shown: (1) no transition in the 0.1 wt% Fe sample at temperatures as low as 1.1° K, (2) a broad transition in the 0.25 wt % Fe sample at 5° K as evidence by a maximum in $(\frac{\partial\mu}{\partial T})_{H\to 0}$, (3) a temperature dependence of the initial susceptibility, $(\frac{\partial\mu}{\partial T})_{H\to 0}$, much stronger than the $T^{-2}$ that would have been expected in the paramagnetic region and (4) $\frac{\partial\mu}{\partial T}$ (H, T) cannot be fitted by a Brillouin function in the paramagnetic region.

Publication

THXXIII L. H. Holley, "The de Haas-van Alphen Effect in Zinc," S.B. Thesis, May 1967.

## 25.0 Investigation of the Structure of Flux Quantization Oscillations

Personnel: R. Meservey, L. Meyers, Boston University

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

In a search for electron correlation effects of higher order than pairs in superconductors, the experiment of Little and Parks has been repeated with some refinements. This experiment involves measuring the resistance of a thin film superconducting cylinder as a function of magnetic field while the temperature is kept at the superconducting transition where the resistance is greater than zero, but less than the normal resistance. Higher order correlations should show up as ahrmonics of the basic flux quantization periodicity of resistance versus magnetic field. In practice we have found that the curves when studied carefully contain a large amount of structure. Although this structure sometimes does appear to have a higher multiple frequency of the fundamental period somewhat as reported by Little, the structure that has been observed with aluminum has been identified with the structure of the resistance versus temperature curves and therefore reflects the sample structure rather than higher order correlations.

26.0 Mössbauer Effect Studies

26.1 Mössbauer Studies of Charge States and Magnetically Induced Quadrupole Interactions

Personnel: J. Chappert, R. B. Frankel, A. Misetich, N. A. Blum (NASA-ERC)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

Multiple charge states, $Fe^{1+}$, $Fe^{2+}$ and $Fe^{3+}$, have been observed in $^{57}Co$ doped MgO and CaO used as Mössbauer sources. The intensity of each charge state depends on the heat treatment of the sample. Heating a $^{57}Co$ doped MgO single crystal at 1500° C in air provides a dominant $Fe^{2+}$ state with Mossbauer line widths of 0.32 mm/sec and 0.43 mm/sec at room temperature and 4.2° K, respectively. When a large external magnetic field, $H_o$, is applied, we observe a hyperfine structure with a quadrupole splitting, $\Delta E$, as predicted recently by Ham. For T = 4.2° K and $H_o$ = 50 kOe (Zeeman splitting larger than strain splitting in Ham's model) we find $\Delta E = 4\epsilon = 0.32$mm/sec. When the magnetic field direction is changed from [100] to [111], the quadrupole interaction changes sign but has the same magnitude, in agreement with theoretical predictions and with experiments on $^{57}Fe$ doped MgO absorbers. Similar effects are observed for $^{57}Co$ doped CaO single crystals.

26.2 Mössbauer Studies of Magnetically Ordered Systems

Personnel: J. Chappert, R. B. Frankel, N. A. Blum (NASA-ERC), M. Schieber (Hebrew University)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

The spin structures of the ferromagnetic spinels $NiFe_2O_4$ and $NiFe_{0.3}Cr_{1.7}O_4$ were investigated by observing the polarization and frequency shift of the $Fe^{57}$ hyperfine lines in external magnetic fields. In a recent letter, Kedem and Rothem have presented zero field Mössbauer data which they claim constitutes evidence for a Yafet-Kittle spin structure in $NiFe_2O_4$. Our measurements show unambiguously that $NiFe_2O_4$ has a Neel structure. We find, however, that $NiFe_{0.3}Cr_{1.7}O_4$ has a Yafet-Kittel structure, and from the measurements we find the angle between the external field direction and the spin direction to be about 21° and 49° for the sublattices A and B respectively. Relaxation effects in the hyperfine spectra in the ferromagnetic state are also observed in this material.

Two similar compounds, $KFe_{11}O_{17}$ and $KFe_5O_8$ have been distinguished from each other by their different Mössbauer patterns at room temperature. Earlier experiments by us as well as by others had apparently been performed on a mixture of the two materials. We have studied the behavior of these two materials in order to ascertain the temperature dependence of the sublattice magnetizations and also the magnetic anisotropy associated with the rotation of the sublattic magnetization.

## 26. 3 Mössbauer Studies in Dilute Alloy Systems

Personnel : R. B. Frankel, D-J Kim, B. B. Schwartz, N. A. Blum (NASA-ERC)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The external field dependence of the hyperfine field at the $Fe^{57}$ nucleus in Pd has been studied up to 140 kOe at temperatures down to 1.2° K using the Mössbauer effect. In a sample for which $T_c < 1.2°$ K and in which the Fe + Co impurity concentration is estimated to be approximately 0.05%, the induced hyperfine field in the saturation region (T < 4.2° K) was observed to increase linearly from -300kOe to -308kOe as the external field was increased from 20 to 130 kOe. This result is consistent with the existence of aknight shift contribution to the hyperfine field on the order of 7%. An attempt has been made to study the effects of impurity-impurity interations by fitting our low $H_o/T$ data to a model recently proposed by Doniach and Murani. Thus far our data is not sufficiently accurate to support or refute this model.

There has been considerable recent evidence for a spin compensated bound state associated with dilute Fe impurities in copper fro which the transitions temperature, $T_K$, was in the range of 5 - 18° K. We have studied the Mössbauer spectrum as a function of external field and temperature, especially the saturation behavior of the induced hyperfine field, i.e., for large $H_o/T$ where $H_o$ is the applied field. We find a very large change in the saturation value of the hyperfine field, which increases from -25 to -52 kOe as the external field is varied from 40 to 136 kOe at 1.2° K. We have shown that the large field variation of the hyperfine field may be associated with the destruction of the spin compensated state and the appearance of an unquenched moment. The implications of this observation for the nature of the possible quenched state in terms of the Kondo theory have been published elsewhere.

## 26.4 Mössbauer Studies Involving Heavy Atoms

Personnel: R. B. Frankel, N. A. Blum (NASA-ERC), L. Grodzins (MIT Physics Dept.)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

The Mössbauer effect has been used to find the magnetic moment of the 99 keV, $3/2^-$ first excited state of $Pt^{195}$. A single line source of $Au^{195}$ in Cu and ferromagnetic Fe-Pt alloy absorbers were used. The g-factor of the state is found to be $(-0.40 \pm 0.10)$nm. The internal field at the Pt nucleus, $H_{int}$(Pt), in the alloy absorbers was simultaneously measured. The internal field was nearly constant, about $1.26 \times 10^6$ Oe, over a range of composition from 3 at % to 30 at % Pt. $H_{int}$(Pt) for an $Fe_{50}Pt_{50}$ alloy absorber and for a source ($Au^{195} \rightarrow PT^{195}$in Fe) was smaller, $H_{int}(Pt) \simeq 1.0 \times 10^6$ and $0.85 \times 10^6$ Oe, respectively.

Extending the measurement of isomeric shifts of nuclear rotational states, the Mössbauer effect has been observed in the 83 keV first excited state in $Eu^{153}$ using a $Sm_2O_3$ source and $Eu_2O_3$ obsorber. Because of the singularly difficult nature of the photon spectrum, a Li-drifted Ge detector was used. Experiments are under way to measure the mean squared charge radius and g-factor or of this level.

Measurements of the isomer shift of the 122 keV $2+ \rightarrow 0+$ transition in $Sm^{152}$ have been completed. From the shift between 2+ and 3+ valence states, a reliable value of $\Delta < R^2 >$ was derived and compared with theory. Mixing of the $\beta$-band into the ground state rotational band was shown to account for only 20% of the observed shift.

### Publications

JP 243 D. Yeboah-Amankwah, L. Grodzins, R. B. Frankel, "Observation of Centrifugal Stretching in $Sm^{152}$", Phys. Rev. Letters 18, 791 (May 1967).

JP 247 R. B. Frankel, N. A. Blum, B. B. Schwartz, K. J. Kim, "Mössbauer Evidence for a Spin-compensated State in Dilute Fe-Cu Alloys", Phys. Rev. Letters 18, 1051 (June 1967).

JP 266 J. Chappert, R. B. Frankel, "Mössbauer Study of Ferrimagnetic Ordering in Nickel Ferrite and Chromium Substituted Nickel Ferrite," Phys. Rev. Letters 19, 570 (1967).

MS 259 M. Schieber, R. B. Frankel, N. A. Blum, S. Foner, "High Magnetic Field Studies of Othorhembic and Rhembohedral $Al_{2-x}Fe_xO_3$ Compounds, 12th Annual Conf. on Magnetism and Magnetic Materials, Washington, D. C., Nov. 1966; J. Appl. Phys. 38, 1282 (March 1967).

JP 287 A. Buyrn, L. Grodzins, N. A. Blum, J. Wulff, "Internal Magnetic Fields at Pt Nuclei in Pt-Fe Alloys," Phys. Rev. 163, 286 (1967).

JP 251 J. Chappert, R. B. Frankel, N. A. Blum, "$Fe^{1+}$ and $Fe^{2+}$ Hyperfine Fields in MgO and CaO," Phys. Letters 25a, 149 (1967).

## 27.0 Electron Interaction in Rare Earth Metals

Personnel: D. J. Kim

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

We have discussed from a unified point of view various aspects of the s-f(s-d) exchange interaction in the ferromagnetically spin ordered states of rare earth metals such as (1) the indirect Ruderman-Kittle-Kasuya-Yosida type exchange interaction between localized 4f spins, (2) the spin wave spectrum of the localized spins, and (3) the interaction between conduction electrons mediated by the exchange of spin waves of the localized spins. The present problem is very similar to that of the electron phonon interaction in metals and to obtain the electron-electron interaction we employ a similar method of using a canonical transformation. The electron interaction obtained leads to a repulsion between electrons of opposite spins at the same atomic site in the vicinity of the Fermi surface. The self energy due to this effective electron interaction is calculated for a simplified model and results in an appreciable enhancement of the specific heat. Actually a large electronic specific heat is observed in most rare-earth metals. For instance in Gd, the specific heat is eight times that given by the free electron model. From a band calculation on Gd, Dimmock and Freeman gave the density of states three times that of the free electron value and attributed the remaining part to the electron-phon interaction effect. It seems fairly possible that our electron interaction mediated by spin waves would contribute to the enhancement of the specific heat.

Publications

JP 226 R. E. Watson, A. J. Freeman, "Covalent Effects in Rare-earth Crystal Field Splittings," Phys. Rev. 156, 251 (10 April 1967).

JP 207 M. D. Sturge, M. H. Crozier, "Is There a Dynamic Jahn-Teller Effect in the $^2D$-E State of $Ce^{3+}$ in $CaF_2$ ?" "Comments" Sect. of J. Chem. Phys., subm. by Bell Telephone Labs., J. Chem. Phys. 46, 4551 (1967).

JP 278 A. J. Freeman, R. B. Frankel, "Hyperfine Interactions", Academic Press, New York, 1967.

## 28.0 Resistivity and Critical Spin Fluctuations in Ferromagnetic Metals

Personnel: D. J. Kim

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

The widely observed anomalous behaviors of electrical resistance of ferromagnetic metals and alloys near their Curie (or Neel) point are shown, based on the Zener model, to be attributed to the critical spin fluctuation in the short range orders of localized spins. The resistance peak at the Curie point in Gd as well as the recently observed logarithmic divergence of $\frac{dR}{dT}$ for Ni at its Curie temperature, is well understood by this mechanism. Detailed comparison between theory and experiment will be developed especially for temperatures below the Curie point.

Publication

MS 353 D. E. Ellis, P. Ros, A. J. Freeman, "Open Shell Hartree-Fock Molecular Orbital Theory of Transition Metal Ion Complexes: $KNiF_3$," 12th Annual Conf. on Magnetism and Magnetic Materials, Washington, D. C., Nov. 1966; J. Appl. Phys. 38, 1377 (March 1967).

## 29.0 Spin Polarization Around a Localized Magnetic Impurity in a Magnetized Metal

Personnel: D. J. Kim, B. Swartz

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Recently neutron diffraction experiments have been used to obtain the spatial distribution of the magnetic disturbance about solute atoms in Pd, Ni, and Fe. These and earlier measurements show that the disturbance produced around a magnetic impurity is quite different for different host metals. For low concentration PdFe alloys the range of the conduction electron polarization about the Fe impurity is large, on the order of 10 A°. In contrast with this long range behavior, the disturbance due to a magnetic solute in ferromagnetic Ni is almost confined to the impurity site. A magnetic impurity in ferromagnetic Fe produces a disturbance intermediate in range as compared to PdFe and Ni. We have completed calculations which correlate the behavior of the disturbance associated with a localized moment and the relative magnetization of the host metal. We find that the range and amplitude of the polarization produced by a magnetic impurity is very sensitive to the relative magnetization of the host metal. The range is large for small relative magnetization (dilute PdFe) and on the order of an atomic distance for nearly complete magnetization (a magnetic solute atom in ferromagnetic Ni where one spin band is presumed full). Furthermore, in dilute PdFe alloys we can account for the sharp decrease, with concentration of the magnetic moment per Fe atom, by considering the increase in the splitting of the host Pd bands caused by adding Fe impurities.

### Publication

Jp 227 Duk-Joo Kim, B. B. Schwartz, "Low Temperature Specific Heat of Dilute Magnetic Alloys", Phys. Letters 24a, 77 (1967).

## 30.0 Spin Susceptibility in Metals

Personnel: A. Misetich, R. E. Watson, Brookhaven National Laboratory; N. Lang, University of California, La Jolla.

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Using the previously calculated bands for Pd metal (A. J. Freeman and J. O Dimmock) we are calculating the spin susceptibility. This work will be used to extend the theoretical calculations on the spin polarization around a localized impurity to the real bands in Pd and will also be used for comparison with the high field susceptibility measurements on pure Pd by Foner.

JP 286 M. C. Passeggi, A. A. Misetich, T. Buch, "Hyperfine Interactions in Many Atom Systems", Molecular Physics 13, 101 (1967).

## 31.0 Correlation Between Electron Spin Resonance and Optical Spectra Under Uniaxial Stress

Personnel: A. Misetich, R. E. Dietz (Bell Telephone Labs); R. Merritt (Bell Telephone Labs)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

We have studied the optical spectra and the electron spin resonance of $Ni^{++}$ in $KMgF_3$ under uniaxial stress. The ground state of $Ni^{++3}$ A2g, splits under uniaxial stress and we have measured this splitting using electron spin resonance. These splittings in the ground state are correlated theoretically with splittings in the excited states, mainly $^3T_{2g}$ which we measured in the optical spectra of these crystals under uniaxial stress. This correlation is used as a test of the limitations of crystal field theory for low symmetry distortions.

### Publication

JP 286 M. C. Passeggi, A. A. Misetich, T. Buch, "Hyperfine in Many Atom Systems," Molecular Physics 13, 101 (1967).

32.0 Theoretical Investigation of the Kondo State

Personnel: H. C. Praddaude, D. J. Kim, B. B. Schwartz

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

A theoretical investigation has been initiated in order to determine the magnetic behavior of the spin-compensated state in dilute magnetic alloys which display a Knodo resistance anomaly. The investigation is concentrating on the high field magnetization, magnetoresistance, and the Mössbauer effect for the Kondo state. Two methods for the theoretical investigation are being used; the two-time Green's function technique using a better decoupling scheme and the Van Hove expansion of the resolvent operator. These investigations will be compared with the various experimental results obtained at this Laboratory on Kondo state materials.

33.0 Dynamics of Electrons in Solids in External Magnetic Fields

Personnel: J. Zak

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

Effective Hamiltonians are usually used for describing the motion of electrons in solids in external fields. The qualitative picture obtained in such a way is of having the motion in the external fields superimposed on the unperturbed motion. We approach this problem by using a quantum mechanical representation that would correspond to this general picture. This representation is obtained by using finite translations in direct and reciprocal space for specifying states. Such a representation enables one to use the coordinate and the momentum on the same footing and it turns out to be very useful for describing the motion of Bloch electrons in external fields. In particular, the derivation of an effective Hamiltonian for the motion of electrons in metals in a constant magnetic field becomes very simple.

Publication

J. Zak, "Finite Translations in Solid State Physics", Phys. Rev. Letters **19**, 1385 (1967).

## 34.0 Magnon Side Bands

Personnel: A. Misetich, R. E. Dietz (Bell Telephone Labs)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Our previous work on the magnon side bands in the optical spectra of antiferromagnets has been extended. We have studied magnon side bands in both absorption and emission spectra of $MnF_2$.

Most of the visible emission in $MnF_2$ occurs at energies smaller than the corresponding transition in absorption. This emission is believed to derive from the decay of excitons trapped on $Mn^{++}$ ions perturbed by various impurities, such as Ca, Zn. Since these localized impurity levels lie a few tens of wave numbers below the intrinsic levels, they form stable traps at low temperatures. This emission consists of a broad phonon side band and a number of zero phonon lines; narrow lines, identified as zero phonon zero magnon decay of localized excitons, and their spin wave side bands. The spin wave side band is a result of the creation of a spin wave simultaneously with the annihilation of a localized exciton.

A theoretical study of the shapes of the spin wave side bands associated with the localized excitions has been completed. As a result we are able to identify the different localized excitons observed in emission and characterize the nature of the coupling between spin wave modes and localized excitons. We have also observed fluorescence resulting from the radiative decay of free excitons, and a magnon sideband of it. The shape of the side band is in excellent agreement with that calculed for a magnon on the same sublattice as the exciton, assuming that the exciton has no dispersion. Such agreement suggests that any exciton dispersion must be smaller than 1 $cm^{-1}$. With respect to the magnon side bands observed in the absorption spectra, we explained the anomalies observed in their shapes, peak positions, and variation with unaxial stress as due to exciton-magnon interaction, since in absorption an exciton and a magnon are created simultaneously and they may interact. However a magnon side band in the emission spectra corresponds to the simultaneous creation of a magnon and annihilation of an exciton, and they do not interact.

## 35.0 New Instrumentation

**Personnel:** L. Rubin, S. Foner, E. McNiff, R. Doclo

**Sponsorship:** Air Force Office of Scientific Research F44620-67-C-0047

### Research Report

Thermometry techniques for measurements in the liquid helium range using resistance and diode thermometers have been improved. New high accuracy read-out instrumentation permits measurements with very low sensor power dissipation and hence a minimum disturbance of the temperature of the system being measured. Improved data handling by digital averaging techniques has facilitated data acquisition and conserved magnet operating time. A 1/H magnetic field sweep system has been developed for de Haas-van Alphn experiments.

A one-shot $^3$He refrigerator system has been developed. Temperatures of 0.35°K with hold times of more than eight hours have been achieved in high field magnets. A vibrating sample magnetometer has been adapted for use with superconducting magnets for very high resolution studies of magnetic moments in weak magnetic materials.

### Publications

JP 223 S. Kurtin, S. Foner, E. J. McNiff, Jr., "AC Superconducting Solenoid for Kilogauss Field Modulation", RSI 38, 600 (May 1967).

JP 236 L. J. Neuringer, R. C. Milward, "Heavily Doped Silicon as a Low Temperature Transmission Filter for the Far-infrared," Applied Optics (Letter to Ed.) 6, 978 (May 1967).

JP 221 H. C. Praddaude, "Development of a 100 kHz Homodyne, 35 GHz Reflection-Cavity Spectrometer with Phase-Lock of the Reference Signal and Low Frequency Field Modulation", Rev. Sci. Instr. 38, 339 (1967).

JP 234 F. Arams, C. Allen, M. Wang, L. Rubin, K. Button, "Far Infrared Laser Measurements," Proc. IEEE, 55, 420 (1967).

MS 320 S. Foner, "Large Volume Helical Pulsed Field Coils - Applications to Synchronous Pulse Operation from 250 - 500 kG." Proc. Intl. Conf. on High Magnetic Fields, Their Production and Application, Colloques Internationaux du CNRS No. 166, p. 385 (1967).

JP 229 S. Foner, E. J. McNiff, Jr., "Calibration and Differential Field Measurement of High Magnetic Fields by Means of a Periodic Size Effect in Gallium", Rev. Sci. Instr., 38, 931 (1967).

## 36.0 Instability in Superconducting Magnets

**Personnel:** J. E. C. Williams, D. B. Montgomery, Y. Iwasa, J. R. Hale

**Sponsorship:** Atomic Energy Commission, AT(30-1)3700

### Research Report

The thermal response of superconducting ribbons and wires carrying current during a flux jump have been studied experimentally and analytically. The ribbons sutdied are $NB_3Sn$ plated with silver and interleaved between cadmium sheets. The temperature of the ribbon following a flux jump is determined by the initial temperature rise, the heat generated by the current and by the ability of the cadmium to act as a heat sink. No liquid helium is assumed present within the winding. Insulation is provided by carefully controlled sulfiding of the silver surface. The sulfiding technique results in a sufficiently small thermal barrier between the ribbon and the cadmium to allow transiently-stable fully-insulated coils of reasonable current density ($2.5 \times 10^4$ amperes/ $cm^2$) to be constructed. Fully insulated coils have the advantage of allowing rapid field changes. A computer study of the thermal response of a coil section immediately following a flux jump agrees well with experimental results and is useful for exploring the relative importance of the parameters as well as the time scale of an instability.

The thermal response of Nb-Ti superconducting wires under flux jumping conditions is now under study. The relative role played by the copper cladding and the liquid helium in contact with the wire during a collapse are being studied experimentally and by computer. In this experiment flux collapses are induced by the application of a small pulse field to the wire while it is in the critical state; magnetization of the sample is monitored throughout the experiment and is used to estimate the maximum temperature reached following the collapse. The analytical model considers the thermal gradients within the superconducting core as well as the nonlinear nature of the heat transfer and the time varying rate of heat generation. It is the aim of the program to determine the amount of cladding necessary to assure stability during a flux collapse.

Work has been completed on the study of the spatially periodic remanent magnetization in superconducting wires following a locally induced collapse of magnetization. When the wire is copper clad, the collapse is uniform rather than periodic along the axis of the wire. In view of this influence of the cladding, it is unlikely that the phenomenon plays a significant role in magnet performance.

Publications

J. E. C. Williams, "High Current Density Superconducting Coils", Intl. Conference on High Magnetic Fields, Grenoble, France, Sept. 1966. Colloques Internation aux DU C. N. R. S., No. 166, Editions DU C. N. R. S., Paris, 1967.

Y. Iwasa and J. E. C. Williams, "The Formation of the Macrovertex Structure in Hard Superconductors", Applied Physics Letters, Vol. 11, p. 58, 1967.

Y. Iwasa, and J. E. C. Williams, "Macrovortices and Transient Stability in Hard Superconductors", Cryogenic Engineering Conference Paper, E-4, Stanford, California, August 1967.

J. R. Hale and J. E. C. Williams, "Transient Stabilization of $Nb_3Sn$ Composite Ribbon Magnets," Appl. Superconductivity Conference, Austin, Texas, November 6-8, 1967. (To be published, J. Appl. Physics).

Y. Iwasa and J. E. C. Williams, "Microvortex Structure in Hard Superconductors", Appl. Superconductivity Conference, Austin, Texas, November 6-8, 1967 (To be published, J. Appl. Physics).

Y. Iwasa, "Stability and Spatially Periodic Magnetization of Hard Superconductors": Ph. D. Thesis, M. I. T., E. E. Department, May 1967 (unpublished).

## 37.0 Flux Quantization Effects in Superconductors

Personnel: R. Meservey, P. Tedrow, L. Meyers

Sponsorship: National Aeronautics and Space Administration NAS 12-101

### Research Report

The quantization of flux in superconductors was predicted in 1950 by London and discovered by Doll and Nabauer and Deaver and Fairbank in 1961. The basic result is that under certain conditions the magnetic flux contained in a superconducting ring is quantized in (mks) units of h/2e. The present study aims to explore flux quantization effects in thin films and their application to the measurement of the properties of superconductors and to other measurement techniques.

To provide the rather complicated thin film structures needed we have equipped a small thin film evaporation laboratory. This contains a high speed pumping station with a multiple source unit and a mask-changing unit for either flat or rotating cylindrical substrates; these systems operate in the $10^{-9}$ Tor region. Auxiliary equipment includes substrate temperature control, film thickness monotors and measuring equipment and optical inspection and measuring instruments.

A study of the amplitude of flux quantization effects in thin film hollow clyinders of aluminum has essentially been completed. In these measurements an unexpected temperature dependence of the magnetic field periodicity was observed. This phenomenon has been explained by a simple model which in addition gives a plausible explanation of why the resistance of such thin-film cylinders can very periodically with the magnetic field. This model allows us to apply the Tinkham theory of the magnetic field periodicity of the free energy to these resistive effects with some confidence. The results to date have agreed well with the Tinkham Theory in amplitude, dependence on film dimension, and angular dependence.

We are investigating the use of flux quantization as a standard of measurement for magnetic field, flux, and electric current. A simple instrument of this kind has been built using a 1 mm superconducting loop, with which it is hoped to achieve an accuracy of a few parts in $10^4$ in measuring the flux quantum (or in determining a current or a magnetic field in terms of the flux quantum). This preliminary instrument is part of the design study of a possible high accuracy instrument. If practical, such an instrument would provide a simple, digital method of obtaining very accurate measurements of magnetic field, flux, current, and even voltage.

## 38.0 Search for Ferromagnetically Trapped Magnetic Monopoles of Cosmic Ray Origin

Personnel: H. H. Holm

Sponsorship: Atomic Energy Commission AT(30-1)3828

### Research Report

The existence of elementary particles carrying magnetic charge was predicted by Dirac in 1931, and appears even more plausible in the light of current theory, despite the failure of several attempts to find them. Dirac "monopoles" may be too massive to have been produced in three synchrotron experiments (Berkely, CERN and Brookhaven), and too rare to have been observed directly among the cosmic radiation. However, incident monopoles may have been accumulating in ferromagnetic minerals, where they would remain permanently trapped with substantial binding energy. Incident monopoles, whether of primary origin or produced by energetic events in the atmosphere, should arrive with energies of $10^{16}$ to $10^{20}$ electron-volts, enough to cause considerable penetration and dispersion in surface rock. A sufficient depth of ocean water, however, would decelerate monoples without immobilizing them and allow them to follow lines of the Earth's magnetic field to the bottom, wher they would be trapped and accumulate near the surface. Sediments from great ocean depth therefore represent the most promising terrestrial source of magnetic monopoles. Magnets generating very intense, continuous magnetic fields have been used to extract monopoles from a variety of materials, and detect them by scintillation counters and nuclear emulsions. Results are as yet inconclusive, and the method is being refined for application to quantities of sediment sufficient to represent a significant area-time product of total cosmic radiation flux. Magnetic monopoles might account for the high-energy component of cosmic radiation, for the observation of "extensive air showers", for the energy emission of "qasars", and for reversals of the Earth's magnetic field as deduced from paleomagnetic studies. They would also provide a theoretical basis for the quantization of electric charge.

Publication

JP 273 H. H. Kolm, "Search for Magnetic Monopoles in Deep-Sea Sediment", Physics Today, 20, No. 10, 69 (1967).

## 39.0 Cooperative Programs

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report

Again in 1967 many groups of Visiting Scientists used the high magnetic field facilities of the Laboratory. Brief descriptions of some of these programs are given here.

Professor J. A. Marcus of Northwestern University and Dr. W. A. Reed of the Bell Telephone Laboratories carried on an extensive study of the magnetoresistance of chromium in fields up to 150 kilogauss. Data on magnetic breakdown in several crystal directions were obtained, but even higher fields will be necessary for a complete description of the phenomenon. Dr. J. Korving of the Kamerlingh Onnes Laboratory, Leiden, Holland, has measured the influence of magnetic fields on the viscosity of polyatomic gases. Measurements on nitrogen, carbon dioxide and carbon tetrafloride show that the magnetic field effect on the viscosity can be described in terms of inelastic collisions only. Professor R. M. Hochstrasser and students from the University of Pennsylvania have continued their studies of the Zeeman effect in optical spectra of molecules. New information was obtained on the lowest triplet state of anthracene and other similar molecules. Professor D. J. Sellmyer and students in the M. I. T. Metallurgy Department have continued their studies of the Fermi surface in alloys by high field magnetoresistance and Shubnikov-deHaas measurements. Dr. H. Roth and coworkers at the NASA Electronics Research Center have studied the high field transport properties of degenerate germanium, silicon and III-V compounds. The critical field characteristics of high field superconductors have studied by group from the Stanford Linear Accelerator Center, Avco-Everett Research Laboratory, Linde Division of Union Carbide and the MIT Metallurgy Department. Professor A. Javan, Dr. S. Iwasa, and students in the M. I. T. Physics Department have used field up to 100 kilogauss and infrared radiation from an amplitude stabilized He-rare gas laser to make magnetoreflection measurements on single crystals of arsenic, bismuth and graphite. The magnetoresistance of crystalline boron was studied by Dr. W. P. Lonc of Loyola College in Montreal.

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SECTION F

INSTRUMENTATION LABORATORY

# INSTRUMENTATION LABORATORY

The Instrumentation Laboratory, a division of the Department of Aeronautics and Astronautics, is a defense research orgaization devoted to research and development in inertial guidance and space navigation systems. The following research on materials was undertaken in support of several of these guidance and navigation contracts.

Sponsorship

The Instrumentation Laboratory is sponsored by a number of agencies of the United States Government, which are listed under each subheading.

# INSTRUMENTATION LABORATORY

## Personnel

Professor C. S. Draper, Professor, Aeronautics and Astronautics, Director, Instrumentation Laboratory
F. E. Houston, Deputy Director
R. Woodbury, Deputy Director
P. N. Bowditch, Associate Director
W. G. Denhard, Associate Director
M. S. Sapuppo, Associate Director
Dr. L. B. Dane, Deputy Associate Director
A. P. Freeman, Deputy Associate Director
E. J. Hall, Associate Director

## Staff Members Participating in Materials Research

Dr. S. Allen
G. Augeri
A. R. Calabrese
R. Colby
A. C. Edwards
C. S. Elder
C. H. Hanson
W. H. Keating
L. L. Kriensky
G. F. MacNeill
J. K. McEwen
R. L. Morey
J. L. Nelson
J. R. Palmieri
M. Roberts
B. Rockower
H. Rowe
R. J. Schiesser
Dr. J. R. Stemniski
K. A. Taylor

## Sponsorship

Listed under subheadings

# RESEARCH IN MATERIALS SCIENCE AND ENGINEERING AT THE INSTRUMENTATION LABORATORY

## 1.0 Joining Beryllium to Uranium-Molybdenum Alloy

Personnel: C. S. Elder, J. R. Palmieri

Sponsorship: AF 33 (615)-2243

Research Report:

A program is being conducted at the M.I.T. Welding Laboratory to develop a method for obtaining sound brazed joints between beryllium and uranium - 8% molybdenum alloy. This low-to-high density material combination is desired in an instrument float.

Based on preliminary spreading tests, unsuccessful results have been obtained using the following brazing alloys: pure aluminum; pure silver; gold-nickel alloy (82 Au, 18 Ni). On the other hand, silver copper alloys (72 Ag, bal. Cu, with or without Li additions) look encouraging. The work is being done under vacuum with an electron beam as a heat source and using titanium vapor deposition pre-treatments to promote wetting. *

## 2.0 Low Friction Surface Using Diamond

Personnel: A. R. Calabrese, J. R. Palmieri

Sponsorship: AF 33 (615)-2243

Research Report:

An attractive property of diamond is its low coefficient of friction against other materials. In an attempt to utilize this feature in a gas

* As described in E-1734 "Brazing of Beryllium," Final Report on DSR Project 9909 by C. M. Adams and S. Weiss.

bearing, work is being done to develop a surface in which a moderate amount of small diamond particles are incorporated with their flat facets oriented parallel to and exposed on that surface.

Several approaches to metallizing the diamonds before surrounding them with a metal matrix are being investigated. Among these are vapor deposition, electroplating, and brazing.

## 3.0 Precision Properties of Gyro Materials

Personnel: J. R. Palmieri

Sponsorship: AF 33 (615)-2243

Research Report:

Micro-mechanical properties evaluation, such as micro-yield stress (the stress required to produce an immediate, small residual strain, usually arbitrarily chosen as one microinch per inch) and micro-creep (a delayed strain--e.g. μin/in/month--resulting from an applied load less than the MYS--e.g. 50% MYS-- at a given temperature - e.g. room temperature), may be affected by the strain measurement method used. The most common techniques used in this field are (1) the bonded filament electrical resistance strain gage, (2) the optical extensometer (Tuckerman Strain Gage), and (3) the capacitance type strain gage. An effort is being made to compare directly data obtained using the first two methods above on several gyro materials (e.g. 2024-T6 aluminum subjected to a heat treatment used for power leads).

## 4.0 Gas Bearing Materials

Personnel: J. K. McEwen, J. L. Nelson, J. R. Palmieri

Sponsorship: AF 33 (615)-2243

Research Report

Hydrodynamic gyro spin-axis gas bearings must be capable of withstanding occasional high-speed contact and repeated low-speed rubbing.

Screening test procedures for materials are being developed that should correlate with service behavior. Some materials under examination are vapor-deposited $Al_2O_3$; cememted $Al_2O_3$; high purity fired $Al_2O_3$; boron carbide; tungsten carbide.

## 5.0 Studies of Materials for Gas-Lubricated Gyro Bearings

Personnel: H. Rowe

Sponsorship: NASA/MSC under Contract NAS 9-4576
Subcontract 349

### Research Report

Data now available on simulated service for gas bearing gyro components and of some service data collected on gyro assemblies have shown the desirability of fabricating the assemblies from high density, small grain-sized materials with a high degree of perfection in the surface finish. The high density and small grain size is essential to achieve high strength in materials in general, and for materials in sliding contact to be resistant to attritive wear, high strength seems to be essential. Furthermore, the frictional drag between sliding surfaces is assumed to be dependent upon the perfection of the mating surfaces. In order to achieve specimens free from pull-outs, high density, small grain-sized samples are required. In order to provide suitable samples for further evaluation of these assumed criteria for improved performance, a program is being conducted at Lexington Laboratories, Inc. to provide materials of the highest density and smallest grain size available, that is: hot-pressed polycrystalline aluminum ozide, and to vapor coat this material with an epitaxial layer of aluminum oxide by means of an isothermal vapor reaction and deposition process. Uncoated hot-pressed material samples will also be provided for xomparison with the vapor-coated blanks. Materials coated previously have not been of the smallest grain size available. The present effort is to carry the improvements heretofore attined into the region of grain size and density presently hypothesized to be best for the desired performance.

## 6.0 Development of Hot Pressed Alumina for Gas Bearing Applications

Personnel: G. Augeri

Sponsorship: Navy/Special Projects under Contract N 00030-66-C-0189
Subcontract 362

Research Report:

This program is concerned with the development of extremely fine grained, high density polycrystalline alumina by vacuum hot pressing techniques. The goal of this study is to effectively control raw material characteristics and processing conditions to enable the realization of alumina gas bearing component shapes of consistent microstructure and physical properties. Specifically, to characterize powders used in hot pressing process for chemical purity, X-ray analysis, surface area measurements, electromicroscropy for particle size, and use of various grain-sized powders to determine effects on processed billet. Develop calcining treatment to drive off impurities such as $SO_4$ as a gas from powder by thermal means. Improve agglomeration techniques sc that the pan-dried or spray-dried processing on the powder will result in reduced bulk volume of the powder prior to hot-pressing and elimination of low density areas in the processed billet. And investigate methods of improving dispersion of MgO (grain growth repressor) in alumina powder for a more uniform billet.

Additional work will be done to improve fabrication techniques along the lines of a cleanliness program to reduce contamination in processed billets, a tooling modification program to improve pressure and temperature distribution in punch and dies, and a costs analysis of the merits of pressing individual shaped blanks versus billets.

## 7.0 Dimensional Stability of Beryllium Oxide

Personnel: E. J. Hall and B. Rockower

Sponsorship: Bureau of Naval Weapons Department of the Navy
Under Contract NO sp 66127-C

Research Report

Tests were conducted at Southern Research Institute, Birmingham, Alabama to determine precision elastic limit and dimensional stability of beryllium oxide specimens under tensile and compressive loads. Results show that cold pressed beryllium oxide material has much higher strength values than hot pressed material. The investigation is continuing to develop a material with a precision elastic limit greater than 15,000 psi.

## 8.0 Vapor Deposition of Arsenic Trisulfide Glass

Personnel: B. Rockower

Sponsorship: Bureau of Naval Weapons Department of the Navy
Under Contract NO sp 66127-C

Research Report:

A procedure was developed to successfully vapor deposit arsenic trisulfide glass on gyro ceramic motor stators. The glass encapsulation is superior to the more conventional epoxy encapsulation on motor stators because of greater rigidity and improved dimensional stability. Also the glass encapsulation will not emit any contaminating gaseous materials after vapor deposition. This procedure is now being used by some gyro manufacturers to manufacture motor stators for flotation gyroscopes.

## 9.0 Synthesis of High Density Gyro Fluids

Personnel: E. J. Hall and B. Rockower

Sponsorship: Department of the Navy, Contract N 00030-66-C-0189

Research Report

The objective of this effort is to synthesize a fluid that has a minimum density of 3 grams/c. c. and a viscosity of approximately 2400 cps at 138$^{o}$F. A high density gyro flotation fluid is desirable in that it makes possible the design of smaller instruments or instruments with greater angular momentum.

During the past year phosphagene type fluids have been synthesized with the required density and viscosity in excess of 4000 centistokes. Work has been devoted primarily to minimize the tendency of the fluid to crystallize. Corrosion tests on gyro materials are now in progress. Other fluid properties which are being determined are coefficient of cubical expansion, Newtonian behavior, pour point and thermal conductivity. Results of thermal diffusion tests show the phosphagene fluid to be superior to bromotrifluoroethylene type fluids currently being used.

10.0 Calculation of the Molecular Diameter and Length of Perhalogenated Gyro Damping Fluids

Personnel: Dr. J. R. Stenniski

Sponsorship: USAF Contract AF04(694)-999
Navy Contract N00030-66-C-0189

Research Report:

The Physical dimensions of poly (bromotrifluoroethylene) and poly (chlorotrifluoroethylene) molecules were calculated using reported bond lengths and atomic radii. The diameter wasfound to be 7.1 Å for $(CF_2CG\ Br)_n$ and 6.8 Å for $(CF_2CF\ Cl)_n$. The length varies with number of repeating units. The length was calculated from the formula $L = n\,M + E_1 + E_2$ where E = 4.15 Å for a $CF_2Br$ - end group, E = 3.85 Å for a $CF_2Cl$ - end group, M = 2.55 Å for both - $CF_2CF\ Br$ - and - $CF_2Cf\ Cl$ - monomer units, and n = number of monomer units. Assumptions must be made as to the chemical composition.

Steric hindrance between fluorine atoms and fluorine and bromine atoms was considered with the result that head-to-head addition of monomers during polymerization is just as favorable sterically as head-to-tail addition. Linkages giving bromine atoms on adjacent carbon atoms will increase the diameter to 8.3 Å and for chlorine atoms to 7.7 Å.

11.0 Investigation of Gyro Damping Fluids by Gel Permeation Chromatography; A Study of the Correlation Between GPC and Thermal Diffusion.

Personnel: Dr. J. R. Stemniski, (Miss) L. L. Kriensky

Sponsorship: USAF Contract AF04(694)-999
Navy Contract N00030-66-C-0189

Research Report:

The gel permeation chromatography program begun las year on the molecular weight distributions of polymeric systems has been directed specifically at telomeric bromotrifluoroethylene damping fluids. Using a Waters Associates (Framingham, Massachusetts) Model 200 gel permeation chromatograph, conditions for the optimum separation of these fluids into components have been achieved. Work is now in progress to determine the physical properties of the separated fractions. An attempt is being made to determine correlations between thermal diffusion analysis and GPC. Thermal diffusion is the method presently used to determine molecular weight distributions. This work is expected to be the subject of a paper to be presented at the Sixth International GPC Seminar in 1968.

Application of GPC to systems such as epoxy resins, lubricants, and adhesives is to be explored also.

12.0 Gyro Fluids

Personnel: Dr. J. R. Stemniski

Sponsorship: USAF Contract AF04(694)-999
Navy Contract N00030-66-C-189

Research Report:

The need for denser damping fluids becomes more critical with each improvement in the inertial measuring unit. Presently used telomeric fluids are not expected to meet the increased demands of the future. Efforts are being continued in an attempt to obtain these advanced fluids with high density and high viscosity from industrial organizations most qualified in synthesis of these materials. A detailed progress report is not available on the efforts of each organization contacted, either because work is still in a preliminary stage or is considered to be of a proprietary nature.

A constant search of the scientific leterature and periodicals is carried out in an attempt to discover possible candidates with desirable fluid properties.

## 13.0 Investigations of the Nature of the Yellow Impurity in Gyro Damping Fluids

Personnel: Dr. J. R. Stemniski

Sponsorship: USAF Contracts AF04(694)-999 and F04694-67-C-0028

Research Report:

Samples of clear, colorless gyro damping fluids which are telomers of bromotrifluoroethylene begin to take on characteristic yellowish-brown color with time, even in tightly capped containers. This color seemed indicative of a change in the composition of the damping fluid, prompting investigation into the nature of the reaction.

Since no foreign substances were introduced into the damping fluid the reaction was postulated to be photochemical or thermal. Samples of fluid were irradiated with ultraviolet light of wavelength 2537 Å. These samples quickly took on the characteristic yellow color which had been previously observed. Repeating the experiment with light of wavelength 3650 Å yielded the same results. These results indicate that the reaction can indeed occur photochemically.

The ultraviolet spectrum of the photochemically induced product reveals that a $\pi, \pi^*$ adsorption is being observed which is characteristic of conjugated carbon-carbon bonds. The $\lambda_{max}$ = 267 m$\mu$, which is consistent with theory. It can be concluded that the decomposition product does indeed contain carbon-carbon double bonds. No attempt was made to isolate or specifically identify the products. Similar results were observed when the sample was thermally decomposed.

It appears that labile bromine atoms can be eliminated either photochemically or thermally to produce unsaturation in the telomeric bromotrifluoroethylene fluids.

## 14.0 Detection of Bromine in Gyro Dumping Fluids

**Personnel:** Dr. J. R. Stemniski

**Sponsorship:** USAF Contract AF04(694)-999

**Research Report:**

It has been observed that the colorless perhalogenated gyro damping fluids undergo a photochemical or thermal reaction, producing a yellow fluid. The presumed reaction is the elimination of bromine to form carbon-carbon double bonds. The presence of double bonds has been demonstrated by ultraviolet spectroscopy. It was desirable to show the simultaneous occurrence of bromine.

Bromine is soluble in perhalogenated polymers, which presents difficulties. This difficulty was solved by releasing bromine into an aqueous solution of potassium iodide which is place above the fluid. Bromine is released as a gas on heating at 65°C. The gas reacts with the solvated iodide as follows:

$$Br_2 + 3\,I^- \rightarrow I_3^- + 2Br^-$$

When starch is added to a solution containing $I_3^-$ ion, a deep blue color results. This was observed.

The sensitivity of the test has been experimentally estimated, indicating that 10 ppm of bromine must be present in the aqueous phase to produce sufficient color to be detected.

Any reducing agent with a half-cell potential would theoretically give a positive test with this procedure since the reaction to produce $I_3^-$ ions is an oxidation-reduction reaction. Iron III, for example, is a possible interfering agent but obviously could not be released into the aqueous phase as a g gas. The degree of heating is relatively mild, which also eliminates the possibility of mixing by thermal agitiation. It can be concluded that in the systems studied, only bromine can be responsible for the observed reactions.

## 15.0 Decolorizing Damping Fluids

Personnel: Dr. J. R. Stemniski

Sponsorship: USAF Contract AF04(694)-999

Research Report:

The yellow color in perhalogenated gyro damping fluids generated by photochemical or thermal mechanism can be removed by column chromatography. Results indicate that percolation over large sized charcoal granules was not effective in removing the colored material. Use of a column packing of activated alumina was found to be more effective and the color was removed completely. No attempt was made to determine the composition of the impurity or whether the physical properties changed drastically.

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# SECTION G

# LINCOLN LABORATORY

# LINCOLN LABORATORY

The Lincoln Laboratory is a center for research and development in advanced electronics, with special emphasis on applications to national defense and space exploration. Summarized here is research in materials and related areas originating primarily in the Solid State Division of the Laboratory.


## Sponsorship

The Lincoln Laboratory is a center for research operated by Massachusetts Institute of Technology with the support of the U. S. Air Force under Contract AF 19(628)-5167.

# LINCOLN LABORATORY
# SOLID STATE DIVISION

## Personnel

Professor A. L. McWhorter, Division Head
Dr. P. E. Tannenwald, Associate Division Head
M. J. Hudson, Division Assistant
E. P. Warekois

## Publications

The work of the Solid State Division is reported in detail in the quarterly "Solid State Research Reports," Lincoln Laboratory, M. I. T. (1967, Nos. 1, 2, 3 and 4).

A. L. McWhorter and J. N. Walpole, "Landau Damping of Magnetoplasma Waves for General Closed Fermi Surfaces, "Phys. Rev. 158, 719 (1967).

J. N. Walpole and A. L. McWhorter, "Nonlocal Effects in Low-Field Helicon Propagation in PbTe, "Phys. Rev. 158, 708 (1967).

P. E. Tannenwald and D. L. Weinberg, "Stimulated Raman Scattering in an Infrared Active, Nontotally Symmetric Vibration of α-Quartz," IEEE J. Quant. Electron. QE-3, 334 (1967).

A. L. McWhorter and J. N. Walpole, "Perturbation Calculation of Band Structure Effects in Low-Field Helicon Propagation," Phys, Rev. 163, 618 (1967).

P. E. Tannenwald, "Mode Pulling in a Stimulated Raman Oscillator," J. Appl. Phys. 38, 4788 (1967).

P. E. Tannenwald, "Stimulated Raman Scattering in Quartz, "Proceedings of the Siberian Academy of Science (in press).

## Theses

H. E. Stanley, "Critical Phenomena in Heisenberg Models of Magnetism," Ph. D. Thesis, Physics Department, Harvard University, January 1967.

M. R. Oliver, "Negative Resistivity Effects in CdTe," MS Thesis, Dept. of Electrical Engineering, M. I. T., June 1967.

# RESEARCH REPORTS

## 1.0 Solid State Theory

Dr. H. J. Zeiger, Leader
Dr. M. M. Litvak, Assistant Leader

### Staff Members

Dr. P. N. Argyres
Dr. G. F. Dresselhaus
Dr. D. C. Hamilton
Dr. J. Hanus
W. G. Hartung
Dr. T. A. Kaplan
Dr. P. L. Kelley
Dr. W. H. Kleiner
Dr. D. M. Larsen
Dr. H. E. Stanley

### Research Assistants

S. R. Chinn, Electrical Engineering
J. Sigel, Physics

### Research Report

An analysis has been made of the temperature-modulated reflectivity spectrum of Ni, from the I. R. to the U. V. Structure in the spectrum has been used to obtain a re-ordered set of theoretical energy bands, which give good agreement with a wide variety of experimental observations in Ni.

An improved variational calculation for donor states in a magnetic field has been developed, which approaches more closely the correct result for the limits of zero-field and very high fields. The calculation has been used to explain the impurity state structure observed in the polaron anomaly experiments in InSb in a magnetic field.

A model for an anomaly in the energy levels of band electrons in a magnetic field due to electron-hole pair creation processes has been predicted. The anomaly is analogous to the polaron anomaly observed due to optical phonon creation processes and should be observable in InSb.

An extension of Hartree-Fock theory in atomic or ionic systems has been made by loosening the restriction that the structure have a symmetry consistent with intuition. It is found that this has the effect of giving a significant increase of Hartree-Fock binding energy in some systems.

The investigation of the propagation of light signals in nonlinear optical media continues. A study of the effects of the nonlinearity on pulse propagation indicates that there will be a self-steepening of pulse shape accompanied by a smearing of the frequency of pulses over a wide frequency range. These calculations help to explain a number of observations made in optically nonlinear materials.

The high-temperature expansion method for the classical Heisenberg model of a ferromagnet has been applied to a number of problems. Spin-spin correlation function and magnetic susceptibility expansions have been obtained for a variety of three-dimensional and two-dimensional structures. A new expansion in terms of powers of the Langevin function shows even more rapid convergence and leads to more reliable estimates of the critical exponent in magnetic susceptibility.

Publications

P. N. Argyres, "The Virial Theorem for the Homogeneous Electron Gas," Phys. Rev. 154, 410 (1967).

P. N. Argyres and E. S. Kirkpatrick, "Quantum Kinetic Equations for Electrons in Random Impurities," Annals of Physics 42, 513 (1967).

G. F. Dresselhaus and M. S. Dresselhaus, "Fourier Expansion for the Electronic Energy Bands in Silicon and Germanium," Phys. Rev. 160, 649 (1967).

J. Hanus, J. Feinleib and W. J. Scouler, "Low-Energy Interband Transitions and Band Structure in Nickel," Phys. Rev. Letters 19, 16 (1967).

T. A. Kaplan and W. H. Kleiner, "Hartree-Fock Theory: Slater Determinants of Minimum Energy," Phys. Rev. 156, 1 (1967).

F. De Martini, C. H. Townes, T. K. Gustafson and P. L. Kelley, "Self-Steepening of Light Pulses," Phys. Rev. 164, 312 (1967).

T. K. Gustafson, P. L. Kelley, and R. Y. Chiao, "Self-Trapping in Media with Saturation of the Nonlinear Index," Proc. Siberian Academy of Science (in press).

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Media," Proc. Siberian Academy of Science (in press).

D. M. Larsen, "Electron-Hole Pair Effects on Landau Levels in InSb," Phys. Rev. Letters 19, 1128 (1967).

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H. E. Stanley and T. A. Kaplan, "Possible Phase Transitions for Two-Dimensional Heisenberg Models," J. Appl. Phys. 38, 975 (1967).

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H. E. Stanley, "High-Temperature Expansions for the Classical Heisenberg Model. I. Spin Correlation Function," Phys. Rev. 158, 537 (1967).

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H. E. Stanley, "Critical Properties of Isotropically-Interacting Classical Spins Constrained to a Plane," Phys. Rev. Letters (in press).

H. E. Stanley, "Dependence of Critical Properties on Dimensionality of Spins," Phys. Rev. Letters (in press).

## 2.0 Electronic Materials

Dr. J. B. Goodenough, Leader
Dr. A. J. Strauss, Associate Leader

### Staff Members

Dr. R. J. Arnott
Dr. M. D. Banus
Dr. R. F. Brebrick, Jr.
A. Ferretti
Mary C. Finn
Dr. G. W. Iseler
J. A. Kafalas
Dr. H. M. Kasper
Mary C. Lavine (part time)
Dr. J. M. Longo
J. R. O'Connor
E. B. Owens
Dr. P. M. Raccah
Dr. T. B. Reed
Dr. F. T. J. Smith
Dr. J. M. Steininger

### Research Assistant

H. I. Andrews, Metallurgy and Materials Science

### Research Report

Improved methods have been developed for growing a variety of single crystals. A furnace has been constructed for pulling crystals from melts produced by the arc-melting technique. Crystals of EuO, NbO, $Ti_2O_3$, and TiC (melting point 3150$^\circ$C) have been grown with this apparatus, which does not require a high-temperature crucible because the melt is contained by a solid shell of the same material in contact with a water-cooled copper hearth. Crystals grown by other methods include $ZnTe_{1-x}Se_x$ alloys, $Cd_{1-x}Mg_xTe$ alloys, $RbNiF_3$, $Ag_3AsS_3$, $CdCr_2Se_4$, and $CrBr_3$.

The phase diagrams of the PbSe-SnSe, Ga-Se, Si-Te, and Bi-Te systems have been investigated by means of thermal analysis, metallographic, x-ray diffraction, and vapor pressure experiments. Hall coefficient measurements on annealed samples of HgSe have been used to determine the homogeneity range and the dependence of carrier concentration on mercury partial pressure.

X-ray diffraction facilities have been upgraded to give more accurate powder intensity data, in order to take advantage of our "simplex" computer program for structure refinement, which includes the correction for the imaginary part of the anomalous dispersion. The improved techniques have been used to solve from powder data the structures of $MnYb_2S_4$, $Nd_2O_2Te$ and $La_4Re_6O_{19}$, and to demonstrate the presence of four electrons occupying an anion vacancy in the presence of four near-neighbor lead atoms in $Pb_2Ru_2O_6$.

We have developed an electronic phase diagram having three coordinates: temperature T, the number $n_d$ of electrons per d orbital, and the transfer energy b connecting localized orbitals on neighboring atoms. It now appears that spontaneous collective-electron magnetism occurs in a relatively narrow transition region $b_c < b < b_m$ on the b coordinate. For $b < b_c$, crystal-field theory and superexchange theory give an adequate description of the magnitude of the atomic moments, magnetic order, the magnetic ordering temperature, and spin-lattice interactions. For $b > b_m$, conventional band theory is adequate. Instead of magnetic order, there is superconductivity at lowest temperatures. In the region $b \approx b_m$, the temperature dependence of the paramagnetic susceptibility changes rapidly with b from a Curie-Weiss behavior with moments approaching localized-electron values to a temperature-independent behavior. In the region $b \approx b_c$, the magnitude of any ferromagnetic moment decreases abruptly with increasing b from $\mu = n_d\mu_B$ to $\mu = (1-n_d)\mu_B$ for $1/2 < n_d < 1$ and from $\mu = (2-n_d)\mu_B$ to $\mu = (n_d-1)\mu_B$ for $1 < n_d < \frac{3}{2}$. Only antiferromagnetic order occurs when $n_d = 1$, but in the range $1/2 < n_d \neq 1 < \frac{3}{2}$ there may be either ferromagnetic, antiferromagnetic, or complex magnetic order and transitions between these types of order may occur as a function of temperature and/or field. A variety of transition-metal oxides and sulfides have been prepared and studied in order to verify the main outlines of this conceptual scheme.

Superexchange theory has been extended to include orbital degeneracies and the possibility of exciton exchange. Structural instabilities due to localized electrons have been characterized and differentiated from those due to collective electrons. In this connection, the semiconductor-to-metal transition in $Ti_2O_3$ was shown to be due to removal of a band degeneracy rather than to antiferromagnetic order. It has been argued that the magnetic ordering temperature versus b should be a maximum at $b_c$, and preliminary pressure experiments indicate that $dT_N/dP > 0$ for localized-electron antiferromagnetism whereas $dT_N/dP < 0$ for collective-electron antiferromagnetism. It is also shown that the apparently contradictory $dT_N/da_o > 0$, which occurs in the two series of perovskites $LnFeO_3$ and $LnCrO_3$, is due to the dominance of changes in Ln-0 covalency effects over changes in lattice parameter $a_o$. Studies of the first-order transition at the Curie temperature $T_c$ of MnAs have demonstrated that a low-spin $Mn^{2+}$ phase is stabilized by P > 4.5 kbar and that there is a sharp change in intra-atomic exchange energy with lattice parameter. This appears to demonstrate a sharply defined $b_c$. Experiments on $LaCoO_3$, though complicated by the simultaneous presence of high-spin and low-spin $Co^{3+}$, indicate a first-order localized-electron to collective-electron transition at $b_c$.

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## 3.0 Solid State Physics

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### Research Report

The research of the Solid State Physics group is primarily experimental and is concentrated in four general areas: electronic band structure, magnetism, scattering phenomena with lasers and high power laser non-linear effects.

In the field of band structure studies, a complete analysis of the HgTe interband magnetoreflection has yielded accurate values for the energy gap, effective masses and momentum matrix element parameter. The study of oscillations in the magnetoreflection of arsenic has given some results which are in contradiction to the Lin-Falicov band model. The beat frequency observed in the Shubnikov-deHaas data on n-type HgSe was explained by inversion asymmetry splitting of the conduction band arising from magnetic field induced effects on the electron orbits. The anomalous exciton fine structure which was observed in the interband magnetoabsorption spectrum of InSb but not of germanium was postulated to arise from the lack of inversion of InSb. Sharper fine structure and additional lines than in the melt grown material were observed in vapor transport grown GaSe. The extension of the electroreflectance technique to low temperatures, by the development of a mechanically integrated package, has allowed the investigation of magnetoelectroreflectance at $1.5^{\circ}K$ in InAs and InSb and the determination of band parameters. The same technique was adapted to electro-absorption so that both electroreflectance and electroabsorption could be simultaneously measured on the same sample and a self consistency comparison could be made by means of the Kramers-Kronig transforms. Extra transitions observed in the electric field modulated magneto-reflection of InSb were attributed mainly to warping of the valence band energy surface and the resulting admixture of close-lying Landau levels. Thermoreflectance studies in nickel at $77^{\circ}K$ have led to a new model of energy band ordering which is consistent with theoretical considerations and also with a number of other experimental observations.

Other magnetic work included a study from liquid helium temperature to $115^{\circ}K$ of the zero field $Cr^{53}$ nuclear resonance in the ferromagnetic state of the spinel $CdCr_2Se_4$ in which the hyperfine field was found to decrease linearly with temperature from $4.2^{\circ}K$ to $77^{\circ}K$. In the continuing study of distant neighbor magnetic interactions in spinels with non-magnetic A-sites, preliminary neutron diffraction measurements in $ZnCr_2Se_4$ indicated a rather complicated spiral pattern at very low temperatures. An investigation of the effect of pressure, up to 5 kilobars, on the magnetic properties of MnAs was initiated. Measurements of the critical point exponents for the para-magnetic susceptibility and the magnetization of $La_{0.5}Sr_{0.5}CoO_3$ gave values which are lower than predicted, respectively, by the high temperature expansion method and the gas-ferromagnet analogy. Antiferromagnetic resonance, in the frequency range 35 to 70 GHz, has been observed in single crystals of $MnI_2$ at liquid helium temperatures where the $Mn^{2+}$ spins order in a flat spiral configuration. Microwave resonance results on $CoCr_2O_4$ as a function of temperature were analyzed on the basis of a molecular field model. The observation and study of spin wave-phonon interaction by means of spin wave resonance in permalloy films at microwave frequencies has confirmed the theory of magnetoelastic coupling and allowed a determination of the coupling constant. In other phonon work, the application of an electric field to InSb has resulted in acoustic amplification at 9 GHz with a net gain of up to 30 db/cm.

Using a 1 watt CW neodymium-doped yttrium aluminum garnet laser operating at 1.06μ, phonon Raman scattering involving the creation of a zone-center optical phonon with subsequent decay through the anharmonic interaction into two acoustic phonons was observed in silicon. Also in silicon, electronic Raman scattering was obtained from phosphorous donor and boron acceptor impurities. Polarization properties and relative intensities of the Raman laser scattering from mixed plasmon-phonon modes in GaAs crystals have been measured and compare favorably with cross-section calculations given in terms of the crystal Raman coefficients which couple the photons to transverse and longitudinal optic modes and to charge density fluctuations. By exciting quartz at low temperatures with a high power Q-switched laser, stimulated Raman scattering was observed from a mode which is both Raman and infrared active; the factors determining the strength of the far infrared radiation, which should be emitted during the stimulated Raman process, were investigated. In another experiment, stimulated Raman emission was obtained in a quartz sample which consisted of a cavity with plane parallel end faces. The mode pattern of such a ruby-pumped Raman oscillator was studied and was shown to exhibit the mode pulling phenomenon usually found in gas lasers.

Stimulated four-photon scattering, or light-by-light scattering, was observed in collaboration with a group at MIT. In other high-power laser research, the spectral power density of the broad frequency smearing which occurs when a high-power Nd: glass laser beam passes through a $CS_2$ liquid cell was studied as a function of input power. A technique was developed for producing high-power pulses of coherent light with frequency continuously tunable over a 1000 Å range. Complementary to the self-focusing studies, a quantitative investigation of thermal self-defocusing, which arises from the passage of a laser beam in an absorbing liquid, was initiated.

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## 4.0 Applied Physics

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### Research Report

Very homogeneous single crystals of $Pb_{1-y}Sn_ySe$ have been grown by the Bridgman technique with compositions in the range $y = 0.0$ to $y = 0.3$. Low carrier concentrations and high Hall mobilities have been obtained by annealing the as-grown material in a two-zone furnace, and the annealed material has been used to fabricate infrared lasers and photovoltaic detectors. Diode laser emission has been observed out to 18.9 μ and photovoltaic response to 22 μ at 12°K. Efficient photovoltaic detectors which operate at wavelengths up to 11 μ and at 77°K have been fabricated from the annealed crystals. Internal quantum efficiencies of about 20% and detectivities in excess of $3\times10^9$

cm/Wsec$^{1/2}$ near the peak at 11 μ have been obtained. The detector response speeds have ranged from less than 5 nsec to nearly 100 nsec and were for the most part not RC limited. The diode lasers fabricated from this material have had output powers in the 15 to 20 μ region as high as 30 mW and external quantum efficiencies up to 5% at 12°K.

Studies on the growth and annealing of $Pb_{1-x}Sn_xTe$ pseudo-binary alloys have yielded highly homogeneous single crystals with carrier concentrations as low as $2 \times 10^{15} cm^{-3}$ and Hall mobilities at 77°K as high as 45,000 cm$^2$/Vsec. Studies of the metal saturated and Te-saturated solidus lines have been carried out as the Sn content, temperature and annealing conditions were varied. Photovoltaic detectors with high quantum efficiencies and high detectivities have been fabricated from annealed Bridgman-grown crystals of $Pb_{1-x}Sn_xTe$. At 12°K internal quantum efficiencies of about 80% and detectivities of between 2 and $4 \times 10^{10}$ cm/Wsec$^{1/2}$ have been observed at the detectivity peak near 17 μ in detectors fabricated from $Pb_{0.8}Sn_{0.2}Te$. The noise in both these and the $Pb_{1-y}Sn_ySe$ detectors appears to be dominated by the Johnson noise of the incremental diode resistance at zero bias. Laser emission from $Pb_{1-x}Sn_xTe$ diodes has been observed at wavelengths out to 17 μ.

The interdiffusion parameters of Pb and Se in PbSe have been studied by introducing controlled deviations from the stoichiometric concentration. Excess Se was diffused into Pb-rich n-type material and excess Pb was diffused into Se-rich p-type material forming in each case a p-n junction. The diffusion constants were obtained by plotting the junction depth as a function of time.

Single crystal CdS platelets have been grown from the elements in a high purity flowing gas system using hydrogen as a reducing agent and carrier gas. Room temperature resistivity of the grown platelets varies from 100 to 0.1 Ω-cm as the growth temperature varies from 750 to 1000°C. Hall mobilities of 360 cm$^2$/Vsec at 300°K and 5000 cm$^2$/Vsec at 77°K have been obtained. Single crystals of ZnTe several millimeters on a side have been grown in a similar system. The temperature of the Zn and Te source material during growth was 700°C with the actual growth occurring at 900-950°C.

A 500 Å silicon layer has been used as an effective etch mask allowing the use of concentrated HF for etching silicon nitride. The silicon is deposited on the silicon nitride in the same silane and ammonia system used initially for depositing the silicon nitride only with no ammonia present. The patterns are etched in the silicon layer using conventional photolithographic techniques. Very good resolution in the resultant silicon nitride pattern has been obtained using this process.

Infrared images in the 4 to 5 μ range have been detected using the radiation sensitive characteristics of a uniform InSb metal-oxide-semiconductor structure. The infrared images are detected by rapidly scanning the device with 0.63 μ light from a He-Ne laser. The detection depends on the highly non-linear photoresponse of the structure whereby the presence of the 4 to 5 μ image affects the signal generated by the 0.63 μ light. In addition, optical information at 1 μ has been read-in and stored for over 1 hour using this same InSb-MOS structure. The information can be non-destructively read-out using 5 μ radiation and erased with 0.25 μ radiation.

A method has been proposed by which infrared radiation is efficiently converted directly to visible radiation by a single solid state device. The device consists of a capacitor-photodetector-photoemitter sandwich in which infrared radiation is incident on one face and the visible radiation is emitted from the opposite face. The low level current produced by the infrared detector is integrated by the capacitor and then delivered to the light emitter in short high current pulses. The feasibility of such a pulsed device has been demonstrated using an indium antimonide diode detector and a gallium arsenide-phosphide diode emitter to convert infrared radiation of wavelengths up to 5.3 μ into visible radiation between 0.6 and 0.7 μ with a quantum efficiency of $10^{-4}$.

Electron beam pumped lasers prepared from single crystal platelets of CdSe grown in an atmosphere of excess Cd have yielded 300 W of peak output power and an internal power efficiency of 38% at 4.2°K. Lasing was observed at decreased power and efficiency up to 100°K. We have also obtained laser emission from ZnTe excited by an electron beam with up to 90 W of peak output power at 5280 Å and 8% overall power efficiency at liquid helium temperature and up to 25 W and 2% overall power efficiency at 77°K.

A 400 KV Van de Graaff accelerator system has been used to implant p-type germanium samples with $As^+$ and $N^+$ ions. The target temperature was varied between 20 and 500°C during implantation. The room temperature $As^+$ implants required post implantation annealing to over 400°C to produce conversion to n-type. However, most of the $As^+$ implants performed in the 450 to 500°C range produced n-type conductivity immediately. To date, the results obtained with $N^+$ are inconclusive.

Type conversion and p-n junctions have been produced in CdTe by implantation of 400 keV $As^+$ ions into n-type CdTe. Each sample was coated with ~1500 Å of $SiO_2$ so that it could be heated to 500 °C during implantation. Following implantation, the $SiO_2$ was removed and each sample was annealed overnight at 650°C with CdTe powder and Cd. Hall effect measurements and d.c. thermal probe tests on these samples indicated that the implanted region was converted to p-type while the unimplanted region remained n-type. The diodes between the implanted and unimplanted regions had sharp reverse breakdowns at 40-50 volts, and in forward bias emitted bandgap infrared radiation.

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Research Report

I. Magnetic Films

1. Uniaxial anisotropy spectrum

The uniaxial magnetic anisotropy spectrum of NiFe films has been studied by means of rotating anneal. In such experiments the magnetization is continuously rotated by means of an external field, causing the anisotropy axis to rotate. The atomic processes responsible for the anisotropy are characterized by relaxation times $\tau_i = \tau_{io}$ exp $(Q_i/kT)$, where $Q_i$ and $1/\tau_{io}$ are the activation energy and attempt frequency, respectively. The anisotropy axis of a given process will tend to lag behind the magnetization by an amount which depends on frequency and temperature. Measurement of this lag angle then leads to a determination of activation energies and attempt frequencies. The anology between this measurement and internal friction experiments should be noted.

The annealing experiments described above have shown that the uniaxial anisotropy spectrum of Ni-Fe films is characterized by a spectrum of from 4 to 8 separate processes. Experimental values for $Q_i$ range from 0.1 to 2 eV, which can be qualitatively accounted for in terms of various noninteracting point defects. However, the observed values of $\tau_{io}$ range from 1 to $10^{-12}$ sec, and cannot be explained by means of noninteracting point defects, for which $\tau_o \simeq 1/\nu_{Debye} \simeq 10^{-14}$ sec. A model has been proposed in which interaction between single - and divacancies during diffusion between oriented traps (e. g. grain boundaries) results in an effective diffusion constant given by $D_{eff} \simeq 24c_1D_2 \exp(E_b/kT)$, where $c_1$ = concentration of single vacancies and $D_2$ and $E_b$ are the diffusion constant and binding energy for divacancies, respectively. This result is valid in the concentration range $10^{-12} \lesssim c_1 \lesssim 10^{-6}$. Then from $\tau_{eff} = (R/\pi)^2 \, 1/D_{eff}$, where R is the trap spacing (e. g. grain size), and using known values of $E_b$ and $D_2$ for Ni, reasonable agreement with experiment can be obtained.

2. Magnetization Ripple and Lorentz Microscopy

By combining the wave optical theory of Lorentz microscopy with a micromagnetic theory of ripple, the apparent ripple wavelength $\lambda$ has been calculated. In contrast to the classical result, $\lambda$ depends on the defocussing distance Z and electron wavelength $\lambda_{el}$. For small Z the classical limit is reached in which $\lambda$ is proportional to the crystallite size; for large Z, $\lambda$ is nearly proportional to the exchange wavelength. For intermediate Z, however, $\lambda \simeq 1.66\sqrt{\pi Z\lambda_{el}}$, independent of all magnetic parameters. As part of a program to test these predictions experimentally, the resolution of conventional Lorentz microscopy has been extended by at least an order of magnitude.

II. Electron Transport

1. Collection Efficiency in Thin Film Metal-Insulator Triodes

Thin film triodes have been fabricated consisting of alternate layers of Al and $Al_2O_3$. Electrons are injected into the base by tunneling through the emitter barrier and then either decay in the base or are collected over the collector barrier. Measurements on such devices yield values of the mean free path of hot electrons in the Al base and the $Al_2O_3$ collector barrier of ~ 150 Å and 10 Å, respectively. Using the value of these measured parameters the collection efficiency $\alpha$ is calculated to be $\alpha \simeq 50\%$. However, the maximum experimental value of $\alpha$ which has been observed is $\sim 10^{-3}$. Experimental and theoretical studies are in process in an attempt to understand this discrepancy.

2. Theory of Surface Potential in Metals

The effect of electron correlation in the surface region of a free electron metal has been examined in the random phase approximation for an interacting electron gas. For the Slater average exchange-correlation potential, the results are qualitatively in agreement with previous calculations starting from the Bohm-Pines decoupling scheme.

It is also concluded that a Slater type average is inappropriate for discussing many problems of physical interest.

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## SECTION H

# CENTRAL FACILITIES OF THE INTERDISCIPLINARY LABORATORY

# CENTRAL FACILITIES OF THE INTERDISCIPLINARY LABORATORY

The central facilities in the Interdisciplinary Laboratory are now well established and are providing an important unifying force as well as making important contributions to the research and training program. We have followed the deliberate policy of whenever possible building around an experienced faculty member who is pursuing an active research program in the particular field. In this way the capabilities of the central facilities are being maintained at the forefront of the art.

The central facilities now operational are described briefly below:

## I. GENERAL SERVICE FACILITIES

### 1.0 Central Analytical Laboratory - Room 13-4139

D. L. Guernsey, DSR Staff, Ext. 3306
W. T. Martin, DSR Staff
L. A. Carrara, DSR Staff
W. W. Correia, Technical Assistant
R. Teitelbaum, Laboratory Assistant

The Central Analytical Laboratory is maintained as a service facility in support of research throughout MIT. Approximately 70 projects from many departments have made use of this service during the past year. It is equipped to perform complete chemical analysis for major and trace constituents of a wide range of inorganic materials.

Standard wet chemical analysis equipment is supplemented with a Sargent Automatic Titrator for repetitive titrations, a Leco induction heated unit and tube furnace for combustion carbon and sulfur determinations and a Conductrometric Carbon Analyzer for low amounts of carbon.

Analyses of gases are made with a Kjeldahl Digestion and Distillation apparatus for nitrogen, a Leco Oxygen Analyzer with gas chromatograph, a Leco Hydrogen Analyzer designed for hot extraction in vacuum, and a Fisher Gas Chromatograph for analysis of furnace atmospheres.

Trace analyses are made with a Beckman Spectrophotometer with Flame Photometer attachment, a Turner Photofluorometer, a Sargent

Polarograph with microrange extender, a Fisher Controlled Potential Electroanalyzer and a Jarrell-Ash 3.4 meter Ebert Spectrograph with recording microphotometer.

Cooperative arrangements make available the facilities of the Lincoln Laboratory Analytical Section and the Department of Chemistry's Microchemical Laboratory. Arrangements can also be made with the Reactor group for neutron activation analysis, with the Electron Optics group for x-ray fluorescence analysis and with the Ceramics group for Differential Thermal Analysis.

2.0 Central Machine Shop - Room 13-1028

P. Kelleher, Foreman, Ext. 6842
E. Newman, Machinist
E. Shmid, Machinist
E. Gempka, Machinist
T. Farrell, Shop Helper
F. Payne, Machinist (Student/Faculty Shop, 13-2045)
C. Desjardin, Machinist

This is a fully equipped general machine shop for general or high precision machining of metals, plastics or ceramics.

There are three milling machines for surfacing, cutting slots, grooves, etc. Two are equipped with optical scales for precise hole boring. All have rotary tables and dividing heads for angular indexing. There is also one horizontal milling machine.

A geared head drill will drill a 1" diameter hole in the center of a 24" circle and will fly cut an 8" diameter in a plate. For cutting plate, there is a metal cutting bandsaw with a 24" throat. Grindable metals can be surfaced on a 6" x 18" surface grinder.

There are four tool-room type lathes that are capable of high precision turning, boring, drilling and thread cutting, including metric pitches. There are also two larger lathes with a turning capacity of 16-1/2"

3.0 Electronic Repair and Construction Service - Room 13-1028

E. L. Greenwood, Project Technician, Ext. 2113

The Electronic Repair and Construction Shop is engaged in the design, construction and testing of new electronic equipment and the repair of many types of electronic equipment and instruments. A valuable service of the facility is consultation with faculty, students and other technicians on their electronic problems.

4.0 Electronic Instrument Loan Service - Room 13-1025

E. L. Greenwood, Project Technician, Ext. 2113

The Instrument Loan Service is closely related to the Electronics Shop and functions under the supervision of the same technician. Instruments of general laboratory utility are periodically added for loan service when short-term needs are encountered.

5.0 Central Computation Facility - Room 13-5145

B. L. Averbach, Professor, Metallurgy, Ext. 3320
R. Kaplow, Associate Professor, Metallurgy, Ext. 3322
J. W. Brackett, Research Associate, Metallurgy, Ext. 6919
Sally Duren, DSR Staff, Ext. 6928

The facility is equipped with an IBM 1050 console, a remote terminal which may be linked to the time sharing system (CTSS) at either the MIT Computation Center of Project MAC. Time sharing users may also utilize an available "ARDS I" storage tube display unit, for dynamic display of graphical and other pictorial information. IBM type 029 and type 026 keypunch units (keypunch) are available for card punching for "off-line" input to the time sharing systems or for batch processing input.

All of the facilities of CTSS are available through the typewriter-storage display console including those which allow program editing, compilation and execution (with languages such as MAD, Fortran and AED). System MAP is also available, which allows a wide variety of mathematical analyses to be performed without any programming. The latter system has been extended and now includes, in addition to previous facilities, a package of efficient matrix operation routines and simple commands for graphical display on the storage tube.

Miss Sally Duren is the programmer associated with the Central Computation facility. Miss Duren is available for consultation regarding the use of the time sharing system and the batch processing system as well as for assistance in actual programming difficulties.

During the past year, many interesting problems have been analyzed with the assistance of the center, often by persons who had little or no previous experience in computer applications. The variety of these, reflecting the wide range of interests within materials research, is evidenced by a brief sampling of topics: the scattering of light from fluids near critical points, structural studies of alloy phases, the effect of pH and metal ion concentration on equilibirum hydrolysis, and the performance characteristics of germanium bolometer detectors.

## 6.0 Materials Center Reading Room - Room 13-2137

Alice McGee Robrish, Librarian, Ext. 6840

The Reading Room has a very selective working collection oriented toward materials science. Immediate availability of items in the collection is of prime concern and it is therefore a reserve collection circulating only during hours that the Reading Room is closed.

There are 850 monograph titles and subscriptions to 80 journals. Normally journal titles include only the last two years of issues.

There is a Xerox facility located across the hall available to those who can charge copies to an operating account.

The services of the Reading Room include literature searching, bibliographies, and aid in maintaining current awareness. A bulletin is periodically published giving an annotated listing of recent acquisitions, library news, and information on science literature. Further, the Reading Room serves as a liaison between Materials Center personnel and the Defense Documentation Center, referral services, and specialized data analysis centers.

## 7.0 Technical Information Services - Room Lincoln D-209

E. P. Warekois, Research Staff, Lincoln Laboratory and National Magnet Laboratory, Ext. 81450

Mr. Warekois provides technical information service on materials to the Center for Materials Science and Engineering, the MIT Lincoln Laboratory and the National Magnet Laboratory.

# II SPECIALIZED SERVICE FACILITIES

## 1.0 Central Facility for Microscopy and Metallography-Room 13-5077

J. F. Breedis, Assistant Professor, Metallurgy, Ext. 6938
R. Goss, Technician, Ext. 2447

The facility is comprised of equipment for metallographic studies using optical microscopy, electron microscopy, and electron diffraction. Routine investigations of short duration may be performed by a technician working for the facility. Instruction in the use of the electron microscope is provided for those who plan more protracted research programs. The personnel of the facility are available for advice on specimen preparation and the interpretation of results.

The equipment available includes a Siemens Elmiskop I electron microscope with high resolution electron diffraction attachment, a Leitz MM5 metallographic microscope, and Spencer and Unitron stereo microscopes. Specimen preparation facilities include two vacuum evaporators and several types of thin foil preparation devices. A photographic darkroom and enlarger is associated with the facility.

## 2.0 Gas Analyzer Mass Spectrometer Facility-Room 8-109

J. F. Elliot, Professor, Metallurgy, Ext. 3305

A gas analyzer is used to analyze the molecular beam from a Knudsen or Langmuir effusion cell. This small mass spectrometer is suitable for the identification of vapor species, and, under limited conditions, for determination of ratios of concentrations of vapor species.

## 3.0 X-ray and Low Energy Electron Diffraction Laboratory-Room 13-2106

D. P. Shoemaker, Professor, Chemistry, Ext. 6827

A General Electric XRD-5 x-ray Diffractometer with two x-ray tubes is available for taking x-ray diffraction photographs as needed for structure investigations or for orienting crystals. If the user does not have his own diffraction equipment, other equipment in the laboratory can generally be borrowed including a back reflection Laue camera with a Polaroid film cassette.

The laboratory also has a Varian Low-Energy Electron Diffraction Unit, complete with test chamber, vacuum system, bakeout oven, and all needed gauges and controls. It can be used for low-energy electron diffraction studies of ultra-clean surfaces of crystals and of chemisorbed layers.

In all cases the user of these equipments is expected to do all his own crystal preparative and manipulative work, supply other needed materials and do his own result interpretation.

4.0 X-ray and Electron Optics Laboratory Facility - Room 13-4009

R. E. Ogilvie, Professor, Metallurgy, Ext. 3311
T. O. Ziebold, Associate Professor, Nuclear Materials, Ext. 6885
J. Adario, Technician, Ext. 6887

The X-ray diffraction central facility will continue to offer the services performed in the past. These services have consisted of teaching graduate students and technicians from other departments in the Institute to carry out routine X-ray diffraction studies. The facility has also used its own personnel to perform the necessary experiments for members of the Institute. Most of this work has consisted of orienting single crystals, identifying unknown materials and precision lattice parameter measurements.

The electron microanalyzer has become a general service instrument for the Materials Science Center. Examples of the work that this instrument is well suited for includes analysis of diffusion couples, distribution of elements in areas of dendritic segregation, identification of inclusions, and the analysis of thin films.

The laboratory has just installed a new scanning electron microscope which will be made available to the members of the Institute. This instrument is well suited for the study of irregular or fractured surfaces.

5.0 Insulating and Optical Crystal Growth Facility - Room 13-3146

A. Smakula, Professor, Electrical Engineering, Ext. 3696
Dr. A. Linz, Research Associate, Electrical Engineering, Ext. 3208
Dipl. Ing. J. Kalnajs, DSR Staff, Ext. 2112
V. Belruss, DSR Staff, Ext. 2192
Dr. R. Mykolajewycz, DSR Staff, Ext. 6878
E. Farrell, DSR Staff, Ext. 3692

Dr. D. Gabbe, DSR Staff, Ext. 3698
K. Bangerskis, Technical Assistant, Ext. 6879
A. Vetrovs, Technical Assistant, Ext. 3692
R. Mills, Technician, Ext. 3697

The facility is equipped to handle three phases of crystal growth and evaluation.

1. Chemical preparation of feed materials of halide, fluoride, and oxides of various types can be accomplished. There are furnaces for calcining oxides in air and various gases, calcination of fluorides under HF atmosphere and the purification of these materials. There is a resistance heated zone refiner for the purification of low melting point fluorides. There is also a dry box for handling deliquescent halides and fluorides and some equipment for pulverizing and classifying flame fusion oxide feeds.

2. The crystal growth facilities include 8 baths for growth from aqueous solution. A Tem-Press 2-reactor system capable of operating at temperatures up to 800°C and pressures of 10,000 p.s.i. is available for hydrothermal growth from aqueous solutions. Halide crystal growth is accomplished with a low-temperature Bridgman furnace using sealed quartz crucibles and two Czochralski furnaces with atmosphere controls. Fluoride crystals can be grown using an RF powered Bridgeman furnace and a graphite resistance-heated NRC pulling furnace. The growth of refractory oxide crystals by melt techniques is accomplished by the use of flame fusion burners and an RF powered high-temperature Czochralski furnace. To grow oxides from solutions of fluxes there is one large and two small flux furnaces and three furnaces equipped with pullers for top-seeded solution growth.

3. Crystal evaluation is the third capability of the facility. Precision density measurements can be made with a recording balance for large specimens and a microbalance for small specimens. Precision measurements of the lattice constant in single crystals as well as powders can be made with a Norelco x-ray unit, a clinometer and an x-ray monochromator. There is also a hardness tester for single crystal evaluation. Optical measurements can be made on a Beckman DK-1 spectrometer and a Cary 14R high-resolution spectrophotometer with ultraviolet, visible and near-infrared ranges. There is also a Beckman IR-12 for the infrared, making possible measurements over the range from 1750A to 50μ. Steady-state fluorescence spectra, excitation spectra and lifetime

measurements can be made over the range from 4000A to 1.2 microns at temperatures between $4^{o}K$ and $500^{o}K$. An electron beam unit also permits cathodoluminescence measurements. X-ray and optical orientation as well as cutting, grinding and polishing of crystals can be carried out. There is also a vacuum evaporator for electroding specimens for electrical measurements and other purposes.

During the past year crystals grown for research within the Crystal Physics Laboratory have included 50 crystals of various oxides such as germanates, $BaTiO_3$, $SrTiO_3$, $KTaO_3$, and $K(Ta,Nb)O_3$ doped with various rare earth and transition metal activators which were grown for optical fluorescence research and laser host studies, and 20 crystals of $(K, Na)TaO_3$ and $K(Ta,Nb)O_3$ which were grown for research on ferroelectricity. Programs are continuing on the growth of rare earth doped $LiYF_4$ and other fluorides for fluorescence studies on laser host materials, and on the development of strain-free crystals of $RbMnF_3$ and other perovskite fluorides for fluorescence and magnetic studies.

Also during this period 13 crystals have been grown or prepared for ten groups from other departments at MIT, and 27 crystals have been produced for 22 research laboratories outside of MIT, which attests to the reputation which has been acquired by the special capabilities of this crystal growth facility.

Extensive use of the Crystal Physics Laboratory facilities by students from other laboratories has been a large factor in this operation.

## 6.0 Semiconducting Crystal Growth and Characterization Facility - Room 13-4122

H. C. Gatos, Professor, Metallurgy and Electrical Engineering
M. Lichtensteiger, DSR Staff, Ext. 2381
W. Fitzgerald, Technician, Ext. 6902
T. Stewart, Technician, Ext. 6904

The Central Facility operation under the supervision of the Electronic Materials Group continues to contribute substantially through its crystal growing facilities, crystal characterization facilities, microscope facilities and high and ultra-high vacuum facilities. Semiconductor single crystals of Ge, Si, InSb, GaAs, GaSb and PbSe were provided to the various groups of the Center for Materials Science, as well as to other groups not located in the Center itself. Services were rendered to the following research groups: Ceramics, Physics of Solids, Electron Optics, Infrared, Semiconducting Device, Chemical Metallurgy and Solid State Physics. In the past year a Bridgman crystal growth facility has been added in which high quality PbSe single crystals have been grown for the Electrical Engineering Department. PbSe single crystal thin films gave been produced by sputtering on sodium chloride and glass substrates.

Characterization of semiconducting materials by means of Hall measurements and resistivity measurements were routinely performed. The facility was also made available to individuals in the various departments for their own research.

The vacuum facility is functioning in two ways, a) by providing advice in the construction and maintenance of vacuum systems and b) by providing high and ultra-high vacuum facilities for the production of thin films and for the investigation of materials under reduced pressure.

The facility is equipped to provide:

Growth from the melt under controlled conditions (pure or doped crystals) of nonvolatile elemental and compound semiconductors.

Growth of materials containing volatile constituents employing two temperature principles (closed systems).

Growth of heterojunctions by back-melting techniques.

Growth by evaporation under reduced pressures.

Growth by vapor transport.

Cutting or dicing of semiconductor crystals with single or multiple cuts.

Polishing of crystal sections.

Electrical characterization by Hall measurements.

Resistivity profiling by macro and micro-four point probe.

Chemical characterization by etching.

Microscope examination by reflected and transmitted light.

## 7.0 Semiconducting Crystal Preparation Facility - Room 13-3023

R. H. Rediker, Professor, Electrical Engineering
R. B. Adler, Professor, Electrical Engineering
W. Pitkin, Technician, Ext. 6844

A semiconductor sample preparation facility has been established. Materials with various physical properties can be cut by judicious choice of the two string saws, the spark cutter, or the diamond cutoff wheels which are available. Facilities for polishing and simultaneously mechanical polishing and etching, and for sandblasting are also available.

8.0 Metal Crystal Growth Facility - Room 8-402

M. C. Flemings, Associate Professor, Metallurgy, Ext. 3233/4
R. Berry, Technician, Ext. 3834

The facility is able to grow high purity metal crystals ranging in melting point from that of lead to that of tungsten, i.e.: 327.43°C to 3370°C. Alloy single crystals of the same metals can also be grown. Controlled orientation of alloy single crystals and bi-crystals can be accomplished and lamellar composite eutectic and eutectic-like crystals grown. Additionally, small to medium size quantities of high purity alloys in polycrystalline form can be prepared.

Equipment used in the facility include an electron beam crystal growing furnace, a high frequency vertical floating zone and horizontal crystal growing unit, a horizontal unit for crystal growing in a magnetic field and several resistance heated inert atmosphere crystal growing furnaces. There is a levitation melting apparatus which includes a splat cooling device. Additionally, there is an induction vacuum melting and pouring furnace and an air melting and pouring furnace.

Other equipment include a Bridgman furnace for crystal growing at $< 10^{-6}$ torr, for crystals of melting point up to 1700°C and up to 2" diameter. An arc melting furnace is available for preparation of small samples of high purity polycrystalline alloy, and for metal crystal growth of alloys and intermetallics of high melting point and high vapor pressure.

During the past year 14 types of crystals have been grown and alloys have been prepared for groups in the Department of Metallurgy, the Department of Mechanical Engineering, and the Department of Physics.

9.0 Metal Crystal Preparation Facility - Room 13-5082

B. L. Averbach, Professor, Metallurgy, Ext. 3320
G. Pishenin, Engineering Assistant, Ext. 6924

The facility has x-ray equipment for the orientation of crystals. The equipment has a Polaroid back which makes it possible to obtain a Laue photograph within a relatively short time.

Crystals are cut on a Felker unit which is equipped with a goniometer and a variety of cut-off wheels. A Servomet spark cutter and a string saw are also available. Since the cutting operation may introduce considerable local damage, metallographic equipment and annealing furnaces are available for the production of strain-free surfaces. Metallographic equipment is available for the examination of the cut surfaces.

The facility's technician either performs all the work or he supervises students who wish to orient and cut their own crystals. Staff members are available for consultation on special problems.

## 10.0 Ceramic Materials Processing Laboratory - Room 4-010

W. D. Kingery, Professor, Metallurgy
R. L. Coble, Associate Professor, Metallurgy
D. R. Uhlmann, Assistant Professor, Metallurgy
F. D. Wilson, Technician, Metallurgy, Ext. 2484

The Ceramic Materials Processing Laboratory is now in its fourth year of operation and is located in Room 4-010.

Additional equipment purchased this year includes a Covel surface grinder with automatic hydraulic feed. This is necessary for grinding the surfaces of hard materials to a high precision.

The processing facility has been a useful one in permitting design flexibility for both students and staff. Significant success has been achieved in making the facility responsive to the needs of the Center, and further progress in anticipated for the year to come.

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