Annual Report 1969-1970

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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(Continued on inside back cover)

ANNUAL REPORT 1969 - 1970

RESEARCH IN MATERIALS

MASSACHUSETTS
INSTITUTE OF TECHNOLOGY

CAMBRIDGE, MASSACHUSETTS

APRIL 1970

Cover: Surface of a single crystal of germanium (X800). The periodic fluctuations in the surface topography constitute growth rate irregularities caused by thermal asymmetry and vibrations. Microphotograph by Professor A. F. Witt, Department of Metallurgy and Materials Science.

OFFICE OF THE PROVOST

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 Science and the School of Engineering, including the Departments of Chemistry, Physics, Civil Engineering, Mechanical Engineering, Electrical Engineering, Metallurgy and Materials Science, Aeronautics and Astronautics, Chemical Engineering and Nuclear Engineering, 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.

March 1970

Jerome B. Wiesner, Provost
Massachusetts Institute of Technology

INTRODUCTION

This is the ninth in the series of Annual Reports on Research in Materials at the Massachusetts Institute of Technology, issued on behalf of the Institute by the Center for Materials Science and Engineering.

The report describes the research conducted at MIT in the field of materials in the academic departments of the Schools of Science and Engineering, the Research Laboratory for Electronics, the National Magnet Laboratory, the Instrumentation Laboratory, and the Lincoln Laboratory.

The research reported in this document was made possible, in part, through support extended the Massachusetts Institute of Technology by various industrial companies and by many agencies of the United States Government. Specific sponsorship is acknowledged in each individual section of each report.

The work in the academic departments and the Research Laboratory of Electronics, Professor H. J. Zimmermann, Director, has been grouped for convenience under the following section headings:

Section A Chemical and Solid State Physics

Section B Electrical, Magnetic, and Optical Properties of Materials and Application to Devices

Section C Metallurgy and Materials Science

Section D Materials Engineering

Much of the above work, but by no means all, has been carried out since 1965 in the Center for Materials Science and Engineering, an interdisciplinary laboratory involving a majority of the departments of the schools of science and engineering. The Center was established in 1961 with the assistance of the Advanced Research Projects Agency of the Department of Defense to promote and support interdisciplinary research and education in materials.

The work in the three special laboratories is presented in the following sections:

Section E National Magnet Laboratory, Professor B. Lax, Director

Section F Instrumentation Laboratory, Professor C. S. Draper, Director

Section G Lincoln Laboratory, Dr. M. U. Clauser, Director

The National Magnet Laboratory operates in many respects in an interdisciplinary fashion; a significant portion of its studies are concerned

with materials and their behavior. The Instrumentation Laboratory, while active in a broad area of applied research and development, also supports some basic studies in materials; these studies and programs are described in this report.

At MIT there are a great many facilities which are intended primarily for support of specific research programs, but which are also available to the entire Institute and to the Center for Materials Science and Engineering for research and teaching in the field of materials. These services and activities supplement in an important way the overall effort in materials research.

The several Central Facilities for materials preparation and evaluation, which were established in the Center for Materials Science and Engineering through ARPA support, permit the production and characterization of a broad spectrum of special materials for an equally broad range of uses; these facilities are not only staffed by experts in the respective fields, but have some of the most modern and efficient equipment available anywhere. These Central Facilities are described in Section H of this report.

The Administrative Office of the Center for Materials Science and Engineering is responsible for issuing this report on behalf of the Institute. Requests for copies of the report should be addressed to Mr. Elwood W. Schafer, Administrative Office of the Center for Materials Science and Engineering, Room 13-2145, MIT, Cambridge, Massachusetts 02139.

This report is possible only through the cooperation and prompt response of the many contributors. Such cooperation has made our task not only an easier one, but a pleasant one.

Nicholas J. Grant, Director
Center for Materials Science and Engineering

March 1970

TABLE OF CONTENTS

Foreword iii

Introduction v

SECTION A. CHEMICAL AND SOLID-STATE PHYSICS

I. Solid State and Molecular Theory Group 1
J. C. Slater, Institute Professor Emeritus, Physics
G. F. Koster, Professor, Physics
P. D. DeCicco, Assist. Professor, Physics

II. Non-Equilibrium Quantum Statistical Mechanics 4
M. O. Scully, Assoc. Professor, Physics

III. Atomic Resonance and Scattering 11
D. Kleppner, Assoc. Professor, Physics

IV. Neutron Diffraction and Neutron Physics Studies 14
C. G. Shull, Professor, Physics

V. The Spectrum of Light Scattered by: 19
Critical Fluctuations in Solids and Fluids; Concentration Fluctuations in Solutions of Biological Macromolecules; and Density Fluctuations in Gases
G. B. Benedek, Professor, Physics

VI. Studies of Critical Phenomena and Order-Disorder Phase Transitions 25
J. D. Litster, Assist. Professor, Physics

VII. The Dynamics of Quantum Fluids 29
T. J. Greytak, Assist. Professor, Physics

VIII. Cooperative Phenomena, Statistical Mechanics, and Solid State Physics 32
H. E. Stanley, Assist. Professor, Physics

IX. Low Temperature Physics - Ultrasonic Study of He^4 Critical Point 46
Dr. R. C. Williamson, Visiting Scientist

X. Semiconductors and Infrared Spectroscopy 48
R. A. Smith, Professor, Physics

XI. Order-Disorder Phenomena 49
C. W. Garland, Professor, Physics

XII. Crystal and Surface Structure Investigations by X-ray, Neutron and Electron Diffraction 54
D. P. Shoemaker, Professor, Chemistry

XIII. Molecular Crystals 57
R. J. Silbey, Assoc. Professor, Chemistry

XIV. Molecular Spectroscopy 59
R. C. Lord, Professor, Chemistry

XV. Microwave Spectroscopy 63
M. W. P. Strandberg, Professor, Physics
R. L. Kyle, Professor, Electrical Engineering
XVI. Optical and Infrared Masers 67
A. Javan, Professor, Physics
A. Szoke, Assoc. Professor, Physics
M. Feld, Assist. Professor, Physics
N. Kurnit, Assist. Professor, Physics

SECTION B. ELECTRONIC, MAGNETIC, AND OPTICAL PROPERTIES OF MATERIALS AND DEVICE APPLICATIONS

I. Solid State Study Group 79
G. W. Pratt, Jr., Professor, Electrical Engineering
M. S. Dresselhaus, Professor, Electrical Engineering
D. Adler, Assist. Professor, Electrical Engineering
D. D. Buss, Assist. Professor, Electrical Engineering
II. Superconductivity Theory 87
L. W. Gruenberg, Assist. Professor, Electrical Engineering
III. Semiconductor Materials and Devices 89
R. B. Adler, Professor, Electrical Engineering
R. H. Rediker, Professor, Electrical Engineering
L. L. Chang, Assoc. Professor, Electrical Engineering
A. C. Smith, Assoc. Professor, Electrical Engineering
R. D. Thornton, Assoc. Professor, Electrical Engineering
B. D. Wedlock, Assoc. Professor, Electrical Engineering
F. O. Arntz, Assist. Professor, Electrical Engineering
J. S. Moore, Assist. Professor, Electrical Engineering
S. D. Senturia, Assist. Professor, Electrical Engineering
D. L. Smythe, Assist. Professor, Electrical Engineering
J. N. Walpole, Assist. Professor, Electrical Engineering
IV. Microwave and Quantum Magnetics 110
D. J. Epstein, Professor, Electrical Engineering
F. R. Morgenthaler, Professor, Electrical Engineering
W. J. Ince, Assist. Professor, Electrical Engineering
V. Crystals Physics and Optical Electronics Laboratory 119
A. Smakula, Professor, Electrical Engineering
D. J. Epstein, Professor, Electrical Engineering
T. G. Davis, Assist. Professor, Electrical Engineering
VI. Particle Optics Laboratory 130
C. K. Crawford, Assist. Professor, Electrical Engineering

SECTION C. METALLURGY AND MATERIALS SCIENCE

I. Physics of Solids 135
B. L. Averbach, Professor, Metallurgy and Materials Science
R. Kaplow, Assoc. Professor, Metallurgy and Materials Science
S.C. Moss, Assoc. Professor, Metallurgy and Materials Science
D. J. Sellmyer, Assist. Professor, Metallurgy and Materials Science
K. H. Johnson, Assist. Professor, Metallurgy and Materials Science
II. Physical Metallurgy 155
M. Cohen, Ford Professor of Metallurgy and Materials Science
J. F. Breedis, Assoc. Professor, Metallurgy and Materials Science
III. Physical Metallurgy 163
M. B. Bever, Professor, Metallurgy and Materials Science

IV. Physical Metallurgy 167
J. W. Cahn, Professor, Metallurgy and Materials Science
K. C. Russell, Assoc. Professor, Metallurgy and Materials Science
V. High Temperature Metallurgy 173
N. J. Grant, Professor, Metallurgy and Materials Science
R. M. Pelloux, Assoc. Professor, Metallurgy and Materials Science
VI. Process Metallurgy and High-Temperature Chemistry 180
J. F. Elliott, Professor, Metallurgy and Materials Science
T. B. King, Professor, Metallurgy and Materials Science
B. H. Rosof, Assist. Professor, Metallurgy and Materials Science
VII. Surface Chemistry 186
P. L. DeBruyn, Professor, Metallurgy and Materials Science
VIII. Metals Processing - Casting and Solidification 189
M. C. Flemings, Professor, Metallurgy and Materials Science
IX. Corrosion Laboratory 194
H. H. Uhlig, Professor, Metallurgy and Materials Science
X. Electronic Materials Laboratory 197
H. C. Gatos, Professor, Metallurgy and Materials Science
A. F. Witt, Assoc. Professor, Metallurgy and Materials Science
XI. Superconductive Materials 209
R. M. Rose, Assoc. Professor, Metallurgy and Materials Science
L. W. Gruenberg, Assoc. Professor, Electrical Engineering
J. Wulff, Professor Emeritus, Metallurgy and Materials Science
J. W. Hafstrom, Assist. Professor, Metallurgy and Materials Science
XII. Ceramics 215
R. L. Coble, Professor, Metallurgy and Materials Science
W. D. Kingery, Professor, Metallurgy and Materials Science
C. J. Mogab, Assist. Professor, Metallurgy and Materials Science
D. R. Uhlmann, Assoc. Professor, Metallurgy and Materials Science
B. J. Wuensch, Assoc. Professor, Metallurgy and Materials Science
XIII. Polymers and Glasses 234
D. R. Uhlmann, Assoc. Professor, Metallurgy and Materials Science
XIV. X-ray and Electron Optics Laboratory 240
R. E. Ogilvie, Professor, Metallurgy and Materials Science
XV. Nuclear Materials Laboratory 245
T. O. Ziebold, Assoc. Professor of Nuclear Materials, Nuclear Engineering

SECTION D. MATERIALS ENGINEERING
I. Mechanics of Ductile Fracture 251
F. A. McClintock, Professor, Mechanical Engineering
A. S. Argon, Professor, Mechanical Engineering
C. A. Berg, Assoc. Professor, Mechanical Engineering
II. Plastic Deformation and Strain Hardening 254
A. S. Argon, Professor, Mechanical Engineering
III. Physics of Strength and Plasticity 256
A. S. Argon, Professor, Mechanical Engineering
IV. Mechanisms of Fatigue Damage in Semi-Brittle Materials at Elevated Temperatures and Fatigue in Composites 257
A. S. Argon, Professor, Mechanical Engineering

V. Mechanics and Physics of Damage in Composite Materials 259
C. A. Berg, Assoc. Professor, Mechanical Engineering
W. J. Shack, Assist. Professor, Mechanical Engineering
VI. Properties of Fiber Composites 262
J. Wulff, Professor, Emeritus, Metallurgy and Materials Science
J. W. Mar, Professor, Aeronautics and Astronautics
VII. Physical and Chemical Properties of Fibers and Polymers 267
S. Backer, Professor, Mechanical Engineering
I. V. Yannas, Assoc. Professor, Mechanical Engineering
VIII. Structural Materials 272
F. J. McGarry, Professor, Civil Engineering
R. C. Jones, Assoc. Professor, Civil Engineering
F. Moavenzadeh, Assoc. Professor, Civil Engineering
S. P. Shah, Visiting Assoc. Professor, Civil Engineering
IX. Surface Properties and Behavior of Materials 296
B. G. Rightmire, Professor, Mechanical Engineering
E. Rabinowicz, Professor, Mechanical Engineering
W. D. Syniuta, Assist. Professor, Mechanical Engineering
X. Surface Properties and Processes 300
R. E. Stickney, Assoc. Professor, Mechanical Engineering
XI. Molecular Beam Laboratory 305
J. P. Moran, Assist. Professor, Aeronautics and Astronautics
H. Y. Wachman, Professor, Aeronautics and Astronautics
L. Trilling, Professor, Aeronautics and Astronautics
XII. Molecular Beam Detector - Adsorbate Sputtering 307
J. P. Moran, Assist. Professor, Aeronautics and Astronautics
XIII. Cryogenic Engineering Laboratory 309
J. L. Smith, Jr., Professor, Mechanical Engineering
H. H. Woodson, Professor, Electrical and Mechanical Engineering
C. Kingsley, Jr., Assoc. Professor, Electrical Engineering
E. G. Cravalho, Assist. Professor, Mechanical Engineering
P. Thullen, Assist. Professor, Mechanical Engineering
XIV. Chemical Engineering of Materials
1.0 Structure - Property Relationships for Membrane Permeation 313
E. R. Gilliland, Professor, Chemical Engineering
S. M. Fleming, Instructor, Chemical Engineering
2.0 Reverse Osmosis Desalinization Membranes 314
A. S. Hoffman, Assoc. Professor, Chemical Engineering
M. Modell, Assist. Professor, Chemical Engineering
S. M. Fleming, Instructor, Chemical Engineering
3.0 Properties of Complex Coacervates of Polyelectrolytes 315
A. S. Hoffman, Assoc. Professor, Chemical Engineering
4.0 Catalysis 316
4.1 Diffusion and Reaction in Porous Materials
C. N. Satterfield, Professor, Chemical Engineering
4.2 Interphase Electronic Interactions in Polyphase Solid Catalysts 319
R. F. Baddour, Professor, Chemical Engineering
M. C. Deibert, Assist. Professor, Chemical Engineering
4.3 Heterogeneous Catalysis 320
R. F. Baddour, Professor, Chemical Engineering
M. Modell, Assist. Professor, Chemical Engineering
5.0 Biomaterials 325
5.1 Non-Thrombogenic Materials
E. W. Merrill, Professor, Chemical Engineering
E. R. Gilliland, Professor, Chemical Engineering
K. A. Smith, Assoc. Professor, Chemical Engineering

E. W. Salzman, M. D., Beth Israel Hospital and Harvard Medical School
W. Gerald Austin, M. D., Massachusetts General Hospital and Harvard Medical School
5.2 Structure and Properties of Elastin 325
A. S. Hoffman, Assoc. Professor, Chemical Engineering
6.0 Cryogenic Chemistry 326
R. C. Reid, Professor, Chemical Engineering
7.0 Crystal Growth and Nucleation
R. C. Reid, Professor, Chemical Engineering
G. Margolis, Assist. Professor, Chemical Engineering
8.0 Radiation Acceleration of Viscoelastic Processes in Polymers 328
E. R. Gilliland, Professor, Chemical Engineering
A. S. Hoffman, Assoc. Professor, Chemical Engineering

SECTION E. FRANCIS BITTER NATIONAL MAGNET LABORATORY 331

1.0 High Field Magnet Development 334
2.0 Cyclotron Resonance in Semiconductors 335
2.1 Quantum Effects in Cyclotron Resonance in p-Type Tellurium 335
2.2 Polaron in Cadmium Telluride 336
2.3 Electron-phonon Interaction in Cadmium Sulfide 336
3.0 Magnetoplasma-optical Phonon Coupling in Polar Semiconductors 337
4.0 Magneto-optical Studies of Semiconductors Using Modulation Techniques 337
5.0 Raman Scattering in Solids 338
6.0 Optical Properties of Europium Chalcogenides 338
7.0 Two-magnon Absorption in Far Infrared Spectroscopy 339
8.0 High Field Magnetic Moment and Field Dependent g-Shift in Cerous Magnesium Nitrate 340
9.0 Exchange Enhancement of Localized Moments in High Susceptibility Pd Alloys 340
10.0 Superconducting and Magnetic Properties of High Temperature Superconductors 341
11.0 Ultrasonic Measurements in Magnetic Materials 342
12.0 Low Temperature Quantum Limit Transport 343
13.0 High Field Magnetoresistance and the Spin-compensated State in Dilute Alloys 343
14.0 Origin of Ferromagnetism in Alloys of NiCu and NiRh 344
15.0 Magnetic Phase Transitions in Antiferromagnetic Systems 345
16.0 Studies of Magnetic Properties of Rare Earth Metals and Alloys 345
17.0 Cyclotron Resonance in Graphite 346
18.0 Magnetic Properties by the Oscillating Temperature Technique 346
19.0 Calorimetric Measurements Employing Oscillating Temperature Technique 346
20.0 Ultra Low Temperature Studies 347
21.0 Mobility of He^4 Ions in Liquid Helium 347
22.0 Properties of Thin Film Superconductors 348
23.0 Spin and Charge Susceptibility of a Ferromagnetic Electron Gas 348
24.0 Localized Impurity States in Metals 349
25.0 Density of States in Palladium 349
26.0 Fluorescence From Intrinsic and Extrinsic Excitons in MnF_2 350
27.0 Electron Interaction and Electronic Structure in Magnetic Metals and Alloys 350

28.0 Mössbauer Effect Studies 351
29.0 Survey of Approximation Techniques for Double Time Thermodynamic Green's Function 352
30.0 Cooperative Programs 352

SECTION F. INSTRUMENTATION LABORATORY 353

1.0 Liquid Lubricants in Vacuum Environments 355
2.0 Materials in Manned Submersible Environments 355
3.0 Materials in Deep Ocean Environments 355
4.0 Investigation of Curing Schedule of Dow 332 Epoxy Resin and BA-1 Activator 356
5.0 Conductivity Measurements of Low Viscosity Fluids 356
6.0 Molecular Weight Distribution Determination of Gyro Damping Fluids by the Thermal Diffusion Method 357
7.0 Properties of Bromotrifluoroethylene Telomer Fluids 357
8.0 Low Temperature Effects on Damping Fluids 358
9.0 Some Applications of Computer Technology to Gel Permeation Chromatography 359
10.0 Heat Transfer Analysis of the M. Fink Thermal Diffusion Column 359
11.0 Accelerometer Fluids 360
12.0 Bromotrifluoroethylene Telomer Gyro Damping Fluids 361
13.0 Single Species Gyro Damping Fluids 362
14.0 Gel Permeation Chromatography 362
15.0 Separation of Damping Fluid Mixtures by Liquid Chromatography 363
16.0 Boron Carbide Surface Studies 363

SECTION G. LINCOLN LABORATORY 365

1.0 Solid State Theory 367
2.0 Electronic Materials 370
3.0 Solid State Physics 375
3.1 Band Structure 375
3.2 Magnetic Interactions and Ordering 377
3.3 Scattering Experiments with Lasers 378
4.0 Applied Physics 381

SECTION H. CENTRAL FACILITIES OF THE INTERDISCIPLINARY LABORATORY 387

INDEX - FACULTY 405

CHEMICAL AND SOLID STATE PHYSICS

I. SOLID STATE MOLECULAR THEORY GROUP

Faculty

J. C. Slater, Institute Professor, Emeritus, Physics
G. F. Koster, Professor, Physics
P. D. DeCicco, Assistant Professor, Physics
K. H. Johnson, Assistant Professor, Metallurgy and Materials Science

Research Staff:

R. Gilmore, Instructor, Physics

Graduate Students:

Y. Cho, Physics
D. Klingspon, Physics
B. Mayes, Physics

Support Staff:

Susan Leonard, Materials Science Center, Secretary

Personnel who have left:

B. Mayes, University of Houston

Degrees Granted:

B. Mayes, Ph. D., Physics, January, 1969

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National Science Foundation, GP-7677, DSR 70607

Research Report

In line with our previous ARPA Reports, we indicate the fields of interest of the members of the group by listing the titles of the contributions to our Progress Reports issued during the year, namely Semi-Annual Progress Reports Nos. 70 and 71 issued on January 15, 1969 and July 15, 1969 respectively.

Contributions to Semi-Annual Progress Reports Nos. 70 and 71

P. D. DeCicco, Compton Scattering of X-Rays in Solids I., 71

R. Gilmore, Construction of Weight Spaces for Irreducible Representations of A_n, B_n, C_n, D_n, 71

R. Gilmore, Spin Representations of the Orthogonal Groups, 71

R. Gilmore, Construction of Weight Space Diagrams, 71

K. H. Johnson, The Electronic Structure of Cesium Chloride Type Inter-Metallic Compounds I. Program of Theoretical Research and Preliminary Relativistic Bands, 70

K. H. Johnson and J. W. Connolly, The Localized Electronic Structure of Crystal Imperfections II. The Bound States of Surface and Line Defects, 70

K. H. Johnson, Scattering Model of Molecular Electronic Structure II. Overlapping Potentials and Correlation Effects Via a Model "Self-Energy" Operator, 71

K. H. Johnson and J. W Connolly, The Electronic Structure of Cesium Chloride Type Intermetallic Compounds II. β' AuZn and β' NiAl, 71

K. H. Johnson and F. C. Smith, Jr., Scattering Model of Molecular Electronic Structure I. Applications to H_2^+, C_2, and LiH, 71

B. W. Mayes, Inelastic Collisions of Electrons with Argon which Excite the $3p^5 4s$ Configuration, 70

J. C. Slater, Present Status of the $X\alpha$ Statistical Exchange, 71

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P. D. DeCicco and F. A. Johnson, The Quantum Theory of Lattice Dynamics IV. Proc. Roy. Soc. A310, 111-119 (1969)

K. H. Johnson, The Energy Bands and Fermi Surfaces of IB-IIB Beta-Phase Alloys, in Energy Bands in Metals and Alloys, (Gordon and Breach Science Publishers, Inc., New York, 1968 p. 105)

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J. C. Slater, Review of the Energy Band Problem with Recent Results, from Energy Bands in Metals and Alloys, L. H. Bennett and J. T. Waber, eds., Gordon and Breach, New York 1968, p. 1-17

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II. NONEQUILIBRIUM QUANTUM STATISTICAL MECHANICS

Faculty:

M. O. Scully, Associate Professor, Physics

Visiting Lecturers:

B. Josephson (Cambridge University)
P. Kwok (I. B. M.)
R. Bullough (University of Manchester)

Research Staff:

D. Kim, DSR Staff, Physics
D. Hyman, Instructor, Physics
F. Hopf, Visiting Scientist
H. Auvermann, Visiting Scientist

Graduate Students:

I. Asher, Research Assistant, Physics
C. Boley, NSF Fellow, Physics
J. Goldstein, Research Assistant, Physics
R. Lang, Research Assistant, Physics
P. Lee, Research Assistant, Physics
J. Paul, Teaching Assistant, Physics
G. Tuthill, Danforth Fellow, Physics
J. Blankinship, Senior Student, Physics
C. Eng, Senior Student, Physics
D. Limbert, Senior Student, Physics
R. Gentala, Senior Student, Physics
J. Stewart, Senior Student, Physics
S. Nagel, Undergraduate Assistant, Physics
J. Rudy, Undergraduate Assistant, Physics

Support Staff:

Susan Leonard, Secretary, Center for Materials Science and Engineering

Degrees Granted:

J. Blankinship, S. B., Physics, June 1969
C. Eng, S. B., Physics, June 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75105

National Aeronautics and Space Administration, Electronics Research Center, NGR-22-009-335, DSR 71450

Research Reports

1.0 Josephson Radiation, Superfluidity and the Laser Threshold Region

Personnel: Professor M.O. Scully; D. Hyman and P. Lee

1.1 The Theory of Josephson Radiation[1,2]

In recent years there has been considerable experimental activity in the study of the superconducting tunnel junction. Among the experiments performed to date are studies of the influence of an external micro-wave field on the junction, measurement of the Josephson radiation line-width, and precise measurements of e/h, the ratio between the electronic charge and Planck's constant. On the more practical side, there has been considerable interest in using the Josephson junction as a micro-wave or infra-red source and detector, although the important problem of overcoming the huge impedance mismatch between the junction and the outside world remains largely unsolved. Theoretical study of the junction, however, has not advanced much beyond the pioneer work of Josephson in 1962. In particular, a classical description of the radiation field has always been used, and the noise properties of the junction, particularly at low temperature, have not been fully studied.

We have undertaken the study of the Josephson junction in some detail. Using techniques developed for the quantum theory of the laser, we have devised a theory that takes into account a quantized radiation field, a resonant lossy cavity, as well as an external DC current. We find that, when we take into account relaxation of the radiation field and the macroscopic "phase" in the superconductor, a slight frequency pulling similar to that in the laser results. We have also obtained the noise spectrum of the voltage across the junction, from which an expression for the radiation line-width is readily obtained. At the present time effort is being spent toward applying field theoretic techniques to the solution of certain aspects of the problem.

1.2 Evaporation from Liquid HeII[3]

The experimental results of Professor J. King and collaborators have raised several questions concerning nonequilibrium processess which occur in liquid HeII. For example, at the time of writing the 1968 technical report, the velocity distribution of vapor atoms was not understood. Stimulated by

considerations, a simple theory of evaporation from liquid HeII was constructed, and used to analyze the experimental results of Johnston and King of the velocity distributions of atoms evaporating from HeII at low temperatures. The Theory suggests that rotons are responsible for shifting the velocity distributions to higher energies. In further investigations, we propose two new experiments that would test our model, and provide new information concerning excitations in liquid helium.

1.3 Analogy Between the Laser near Threshold and a Second Order Phase Transition[4]

The quantum theory of a laser oscillator has been the subject of recent theoretical and experimental activity. The problem is basically to understand the nonequilibrium statistical dynamics of the (single mode) laser field as it interacts with the lasing medium. The physical situation is of a sufficiently complex nature to contain many aspects of a many-body problem, but it is simple enough to permit, to a good approximation, a complete solution. It seems therefore attractive to consider whether the insight gained in the laser analysis can be usefully related to other problems in nonequilibrium statistical mechanics.

A natural comparison may be made between second order phase transitions, such as the order-disorder transitions of ferromagnetic and ferroelectric materials or the vapor-liquid transition of a pure fluid, and the laser near threshold. It is well known, for instance, that the state of a laser changes abruptly upon passing through the threshold point. This point is characterized by a threshold population inversion. The laser field fluctuations becomes progressively larger, whereas the decay time of the fluctuations becomes longer, as the threshold is approached.

The physical basis for this similarity becomes evident when it is recalled that the usual treatments of laser behavior are self-consistent field theories. In the laser analysis we assume each atom evolves (develops a radiating dipole) in an electromagnetic field due to all of the other atoms, and then calculate the field produced by many such evolving atoms in a self-consistent fashion. In this way the laser problem is similar to that of a ferromagnet in which each spin sees a mean magnetic field due to all the other spins and aligns itself accordingly, thus contributing to the average magnetic field.

Following this point of view, we have shown that the laser theory can be discussed using the language of second order phase transitions. Furthermore, in order to emphasize the analogy between a ferromagnetic phase transition and the laser threshold region, the laser theory is extended to include the effects of a classical injected signal, which corresponds to an externally applied

magnetic field in the ferromagnetic problem. A physical review paper is presently being prepared.

2.0 Coherence and the Interaction of Radiation with Matter

Personnel: Professor M. O. Scully; D. Kim, J. Goldstein, R. Lang

2.1 Description of a Many Atom System in terms of Coherent Boson States[5]

Many interesting aspects of atomic physics are associated with atomic coherence, for example, Dicke's superradiance, optical pumping, photon echo, self-induced transparency, etc. The coherence properties of a quantized radiation field have been recently described in terms of the so-called coherent states of a harmonic oscillator. These states have provided a natural basis for description of coherence phenomenon in the theory of laser and Jospehson oscillators as well as certain aspects of superfluidity. In this work we demonstrate how the correlated or superradiant states of a N-atom or N-spin system can be described in a convenient and (hopefully) pedagogical fashion in terms of coherent states of a boson field. We have shown that this description of the system provides us with the closest analog to the classical limit. The macroscopic dipole operator in the coherent state representation is shown to obey the Block equation in which each of the three components is simultaneously well defined.

2.2 On the Coherence Properties of Scattered Light[6]

The scattering of light has long been a useful method of studying the properties of various materials. New experimental techniques, such as the use of lasers as sources of highly coherent incident radiation and photo detection of the scattered light, make possible the study of higher order correlation properties of the scattered radiation; for example, the work of Professor Benedek and co-workers. In the present work we are concerned with some of the correlation characteristics of the scattered light as calculated from various models of the physical processes involved.

The lack of perfect homogeneity in a pure substance is caused by thermal fluctuations. Fluctuations change the value of the local dielectric constant of the medium and so produce the scattering. The scattered electric field may be shown to be directly proportional to the dielectric constant fluctuation (the deviation of the local value of the dielectric constant from its mean value, averaged over the entire substance), and the thermodynamic theory of fluctuations indicates that the dielectric constant fluctuation may be thought of as a random variable with a Gaussian probability distribution. Hence, one expects that the scattered electric field may also be considered a Gaussian random variable.

This result supports the intuitive notion that since the total scattered field is the sum of fields produced by a multitude of local dielectric constant fluctuations, occuring within a sample of macroscopic size, by the central limit theorem of statistics, the total field ought to have a Gaussian probability distribution regardless of the statistics of the dielectric constant fluctuation in each separate small region.

In the present work, this idea is examined for some particular scattering processes without directly using either thermodynamic fluctuation theory or the central limit theorem. The statistical properties of the scattered light is examined by evaluating various electric field correlation functions. Presently, we are investigating the properties of light scattered from a system near its critical point.

3.0 Self-Induced Transparency and Coherent Pulse Amplification

Personnel: Professor M. O. Scully; F. Hopf, H. Auvermann, I. Asher, R. Gentala

3.1 Transient Pulse Behavior and Self-Induced Transparency[7,8]

Using the theory developed in order to deal with coherent pulse amplification, the dynamics of self-induced transparency in an inhomogeneously broadened attenuator is investigated with a special emphasis on delay times. One finds a strong dependence of delay times on the input value of the area parameter θ with pulses of $\theta_{in} \approx \pi$ exhibiting much larger delay times than for $\theta_{in} = 2\pi$. This investigation is extended to include the effects of an atomic phase memory time T_2 which is of the order of 10 times the pulse width (i. e. in accord with current experimental circumstances). The variation of other parameters has been considered, and a method of measuring θ directly is discussed.

3.2 Coherence in the Amplification of Short Pulses (Experimental)

Progress is being made in conjunction with the NASA Cambridge group on setting up experiments to check our theoretical predications[7]. A Fabry-Perot etalon and camera to photograph the mode structure of a Nitrogen cooled laser has been set up. Measurements on single pulses should be made in the near future.

4.0 Phonons

Personnel: Professor M. O. Scully; F. Hopf, I. Asher

4.1 Acoustoelectric Amplification

As discussed in the 1968 report, the amplification of acoustic waves in a piezoelectric semiconductor is being treated as a self-consistent field problem. In continuing our analysis, it has been found essential to include the electron velocity distribution in the calculation. Nonlinearities from any simpler model merely increases the first order gain, and lead to neither hole-burning or saturation.

The present calculation uses a Maxwell-Boltzman distribution to initially describe the electrons in the CdS rod. The resulting integrals are rather complex and can only be evaluated numerically. A program to carry out the calculation has been written using a double-precision Gaussian/Hermite quadrature integration subroutine (the most accurate available) of 64 points. Output includes gain and saturation parameters, steady state power, and steady state frequency pulling.

4.2 Coherent Phonon Pulse Propagation[9]

Recent experiments using phonon pulses to investigate the self-induced transparency (S. I. T.) effect has necessitated some theoretical work to determine the effect of a second pass through the active medium. The theory necessary for these calculations has been developed and the resulting equations are solved by numerical integration. The S. I. T. effect in a two-pass system is presented using delay times and attenuation curves. The modification of these curves with changing T_2 and T_1 are indicated. Other problems associated with a pulse interacting with a medium modified by a previous pulse are discussed. In particular, the questions of gain and absorption of the second pulse and of the direction of the second pulse are treated. Also discussed are the measurements of T_1 using multiple-pass techniques, and the possibility of using these phenomena in a practical application to optical logical circuitry.

5.0 Some Time Dependent Problems in Radiation Theory

Personnel: Professor M. O. Scully; D. Kim, D. Limbert

5.1 Temporal Dependence of Laser Statistics

Work is proceeding toward obtaining the laser photon statistics as a function of the time lapsed since the laser was started. A direct calculation for the density matrix elements $\rho_{n,n}(t)$ has been carried out for certain cases. The time dependence of the moments $\langle n(t)^m \rangle$ has been obtained by numerical integration and are in good agreement with experiment.

5.2 Influence of a Classical Driving Field on the Spontaneous Emission of An Excited Atom

We are presently investigating the spectral distribution of spontaneously emitted radiation from an ensemble of atoms which are driven by a strong, near-resonant classical field. Each atom is taken to have two relevant excited states, one of which is assumed to be metastable. When these two states are strongly coupled by a driving field, spontaneous emission from the excited state to a third (ground) state is significantly modifield. The spontaneous emission spectra from these two states to the ground state is to be obtained by means of a Weisskopf-Wigner type of approximation.

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III. ATOMIC RESONANCE AND SCATTERING

Faculty:

D. Kleppner, Associate Professor, Physics

Research Staff:

Dr. D. E. Pritchard, Instructor, Physics

Dr. M. T. Myint, D.S.R. Research Staff, Center for Materials Science and Engineering

Graduate Students:

G. M. Carter, Research Assistant, Physics

F. Y. Chu, Research Assistant, Physics

G. A. Hawkins, Carl Taylor Compton Fellow

E. Mattison, Research Assistant, Physics

F. G. Walther, Research Assistant, Physics

F. P. Winkler, National Science Foundation Predoctoral Fellow

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and Engineering

Degrees Granted:

G. M. Carter, S. M. February, 1969

Sponsorship:

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

Office of Naval Research, N 00014-67-A-0204-0006, DSR 70314

National Science Foundation, GP 13633, DSR 71799

Advanced Research Projects Agency, SD-90, DSR 75107

1.0 Low Energy Photon Counter

Personnel: Professor D. Kleppner; Dr. M. Than Myint, G. A. Hawkins

Research Report

We are investigating the feasibility of a thin film superconducting device intended to respond to energy pulses of 1 eV or less. A sensitivity of 1 eV would permit it to count hydrogen atoms by detecting their reaction energy when they undergo chemical combination on the detector's surface. Conceivably, the sensitivity will be 0.1 eV or less, in which case the device could operate as an infrared photon counter. This would provide an increase in sensitivity of many orders of magnitude over present infrared detectors. Applications for such a device would be numerous.

We have successfully detected the energy loss of penetrating alpha particles. In order to investigate operation of the detector at lower energies we have constructed a field emission electron source which produces electrons with a rate and energy which can be varied independently. Our initial attempts to detect 300 eV electrons were successful, and we are continuing work towards lower energy.

2.0 Magnetic Moment of the Proton

Personnel: Professor Daniel Kleppner; Frederick G. Walther, P. Frank Winkler

Research Report

The goal of this project was to measure the ratio of the magnetic moment of the proton to that of the electron in hydrogen to an accuracy of 1 part in 10^8. This work is now completed: the final result is $g_j(H)/g_p(H) = 658.210705(6)$ where the uncertainty is three times the statistical error and represents an estimate of possible systematic effects. This result represents an improvement over the best previous measurement by a factor of 30.

The hydrogen maser used for this work is currently being modified to operate with deuterium. Experiments in progress include measuring $g_j(D)/g_p(D)$, and $g_j(H)/g_j(D)$.

3.0 Spin-Exchange Scattering

Personnel: Professor D. Kleppner; Dr. D. E. Pritchard, Frank Chu, Gary M. Carter

Research Report

We have completed our investigation of non-symmetric alkali-alkali collisions. This work has yielded accurate values for the well depth and position of the triplet potential, and information on the exchange potential between alkalis. It has also shed light on a controversy between the experimental and theoretical values of the alkali van der Waals constant. The spin-exchange scattering studies are currently being extended to alkali-molecule collisions.

Theses:

Gary Milton Carter, "Spin Exchange Collisions Between Alkali Atoms and Targets of Arbitrary Spin is a Uniform Magnetic Field, February 1969.

Publications:

D. E. Pritchard, "New Experimental Evidence on the Van der Waals Interaction Between Alkalis," Proceedings of Sixth International Conference on the Physics of Electronic and Atomic Collisions, M.I.T. Press, 1969.

D. E. Pritchard, G. M. Carter, F. Y. Chu, and D. Kleppner, "Differential Spin Exchange Scattering Between Alkali Atoms," Proceedings of Sixth International Conference on the Physics of Electronic and Atomic Collisions, M.I.T. Press, 1969.

D. E. Pritchard, D. C. Burnham, G. M. Carter, and D. Kleppner, "Thermal Energy Crossed Beam Apparatus with Polarized Beams," Proceedings of Sixth International Conference on the Physics of Electronic and Atomic Collisions, M.I.T. Press, 1969.

D. Kleppner, R. F. C. Vessot and N. F. Ramsey, "An Orbiting Clock Experiment to Measure the Gravitational Red Shift, Astrophysics and Space Science 3, to be published.

D. Kleppner, "Experiments with Atomic Hydrogen," Proceedings of the 1969 Institute for Theoretical Physics, Brandeis University (to be published).

IV. NEUTRON DIFFRACTION AND NEUTRON PHYSICS STUDIES

Faculty:

C. G. Shull, Professor, Physics

Research Staff:

W. Just, DSR Staff, Physics

Graduate Students:

C. S. Schneider, Research Assistant, Physics
R. C. Maglic, Research Assistant, Physics
A. C. Nunes, Research Assistant, Physics
C. Stassis, Research Assistant, Physics

Personnel who have left:

R. Maglic (Now Argonne National Laboratory, Argonne, Illinois)
A. C. Nunes (Now Brookhaven National Laboratory, Upton, New York)
W. Just (Now Vienna, Austria)

Sponsorship:

U. S. Atomic Energy Commission, Contract AT(30-1)-3031, DSR 71564
National Science Foundation, Grant GP-8303, DSR 70981

Research Report

1.0 High Temperature Study of Iron Magnetic Scattering

Personnel: R. C. Maglic
Sponsorship: National Science Foundation

The polarized neutron diffraction technique has been used to study the ferromagnetic scattering by iron crystals up to the Curie temperature of 770° C. A high temperature vacuum furnace with temperature control to 1° C was mounted in the vertical field magnet gap on the polarized beam spectrometer. Great care was taken to study extraneous effects that can enter into the measurements such as (a) the effect of simultaneous Bragg reflections, (b) the temperature dependence of extinction occuring in the specimen crystal and (c) the temperature dependence of neutron depolarization occuring within

the crystal. Measurements on the (110) reflection, which is insensitive to changes in the spin density asymmetry, showed a temperature dependence slightly elevated above the accepted bulk magnetization. In contrast to this, previous Mossbauer measurements have fallen somewhat lower than the magnetization. This is not surprising since the three independent measurements reflect different quantities: neutron scattering senses the localized 3d electron magnetization, bulk magnetization corresponds to the total magnetization of all electron groups, and Mossbauer measurements correspond to the hyperfine field at the nuclear site produced by all electronic processes. Further measurements were performed on the (222) and (400) reflections which are very sensitive to changes in the spin density asymmetry around the nuclear site in the unit cell. These measurements indicated essentially no change in the asymmetry parameter as the temperature was elevated to T_c.

2.0 Studies of (222) Forbidden Reflections in Germanium and Silicon

Personnel: A. C. Nunes
Sponsorship: U. S. Atomic Energy Commission

A neutron study of the (222) Bragg reflection in germanium and silicon was carried out at temperatures up to 500° C. This Bragg reflection is normally forbidden (zero intensity is expected) by the lattice symmetry, which is that of the diamond structure. However, a number of x-ray experiments have shown the presence of a finite intensity which has been given interpretation in terms of (1) a non-centrosymmetric distortion of the electron charge density within the atoms or (2) a non-centrosymmetric type of thermal oscillation of the atom centers. An equivalent observation with neutrons would sense only the second of these interpretative models. Past experiments with neutrons have shown zero intensity at room temperature. The present study was directed at improving the sensitivity of the neutron observations and elevating the crystal temperature thereby enhancing the magnitude of the effect. Perfect crystals of silicon and nearly-perfect crystals of germanium were used and great care was expended in removing contaminating intensity effects that can arise from high-order wavelength components and from the presence of simultaneous reflection effects occuring in the crystal. Again even at temperatures as high as 500° C the neutron experiments have failed to detect finite intensity and only an upper limit can be placed on the magnitude of the structure factor. This upper limit can be used to place an upper bound on the magnitude of anharmonic terms in the description of the potential energy that an atom sees in the unit cell. For either silicon or germanium this limit is

considerably smaller than that calculated using an Einstein model that accounts for the measured specific heat and thermal resistivity. It is also somewhat smaller than that expected by analogy with measured values in CaF_2 and UO_2 by Dawson and Willis.

3.0 Study of the Kondo Effect in Cu-Fe Alloys

Personnel: Professor C. G. Shull, C. Stassis
Sponsorship: U. S. Atomic Energy Commission

Polarized neutron scattering is being used to sense the development of the Kondo ordered state in dilute Fe in Cu alloys. It is thought that the iron impurity magnetic moment becomes compensated at low temperature by a conduction electron cloud of opposite spin polarity. Neutron scattering studies to date have been concentrated on single crystals of 1000 parts per million Fe composition. Through application of an external magnetic field of 15 kilooersteds, the induced localized magnetization results in a magnetic scattering which is sensed by its coherence with the nuclear scattering in Bragg reflections. Thus the modification of the field-induced localized moment as the temperature is reduced through the Kondo temperature can be investigated. Present measurements have indicated (a) a substantial reduction of magnetic scattering at low temperature in close agreement with the temperature dependence of the susceptibility and (b) a Kondo ordering temperature of about 10° K. Detailed interpretation of the results must await susceptibility measurements on the present specimens (these are being carried out in Professor Sellmeyer's laboratory) and on further neutron scattering measurements on other Bragg reflections and on other composition alloys.

4.0 Study of Pendellosung Fringe Structure in Bragg Reflections of Silicon Crystals

Personnel: Professor C. G. Shull
Sponsorship: U. S. Atomic Energy Commission

During the past year, one of the neutron diffraction spectrometers at M. I. T. has been modified to permit further studies of the Pendellosung fringe structure in Bragg reflections from perfect crystals. The spectrometer is operated without a monochromating crystal and white, full spectrum radiation is delivered through a long, narrow collimator (divergence about 3 minutes of arc) to the test crystal. Radiation is passed into the crystal (in Laue

arrangement with diffracting planes perpendicular to the entrance and exit faces) through a fine slit opening fabricated with tapered gadolinium edges for high neutron absorption. An equivalent slit opening is used on the exit face with micrometer-controlled position for scanning across the fringe structure within the Bragg reflection. With this system, fringe characteristics have been measured over essentially the full spectrum from 0.6 Å to 1.6 Å wavelength. The Pendellosung fringe structure arises from interference action within the crystal of coherently split beams and the path length within the crystal must be carefully controlled. Considerable improvement in the means of obtaining accurately parallel and flat surfaces without mosaic structure has resulted from the use of a new chemical polishing technique employed in Professor Witt's laboratory. Present experiments have been directed at establishing whether the neutron coherent wave front in passing through the crystal is to be characterized as planar or spherical. Theory predicts a small difference in the fringe characteristics for the two cases and it is necessary to settle this fundamental question before the fringe structure can be used in a precision determination of the silicon scattering amplitude.

5.0 Neutron Diffraction by Crystals of InSb

Personnel: Professor C. G. Shull and W. Just
Sponsorship: National Science Foundation

Crystal slices of InSb have been examined in a double crystal spectrometer to study their intrinsic rocking curve widths and the anomalous transmission that should occur when they are in Bragg reflection. Two matched slices with (220) planes in transmission exhibited a rocking curve width of 1.35 seconds of arc (full width half maximum intensity) for a neutron wavelength of 1.6 Å and this compares quite favorably with the calculated value of 1.18 seconds from Darwin width evaluation. Thus the crystal slices can be considered nearly perfect in so far as satisfying dynamical diffraction theory criteria. A double detecting system was arranged at the spectrometer so that the transmitted beam through the second crystal could be studied simultaneously with the Bragg beam. Traverses of the Bragg angle through the reflection showed the characteristic asymmetrical intensity distribution in the transmitted intensity with higher intensity on the smaller angle side and lower intensity on the larger angle side. Since InSb offers moderate absorption for neutrons, this demonstrates the modification of true absorption under near Bragg conditions as predicted by dynamical theory. The quantitative interpretation of the measurements is being pursued.

Theses

C. S. Schneider, "The Forward Magnetic Scattering Amplitude of Iron for Thermal Neutrons by Prism Refraction", PhD, Department of Physics, February 1969.

R. C. Maglic, "Temperature Dependence of the Thermal Neutron Magnetic Scattering Amplitude," PhD, Department of Physics, June 1969.

A. C. Nunes, "A Neutron Diffraction Search for Noncentrosymmetric Thermal Oscillations in Germanium and Silicon", PhD, Department of Physics, June 1969

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V. THE SPECTRUM OF LIGHT SCATTERED BY: CRITICAL FLUCTUATIONS IN SOLIDS AND FLUIDS; CONCENTRATION FLUCTUATIONS IN SOLUTIONS OF BIOLOGICAL MACRO-MOLECULES; AND DENSITY FLUCTUATIONS IN GASES

Faculty:

G. B. Benedek, Professor, Physics

Research Staff:

V. DeGiorgio, NATO Fellow

M. Giglio, Visiting Scientist, Center for Materials Science and Engineering

J. B. Lastovka, D.S.R. Staff, Center for Materials Science and Engineering

D. Schaefer, National Science Foundation Fellow and Sloan Foundation Fellow

P. Schofield, Visiting Professor, Department of Physics

J. Zollweg, National Science Foundation Fellow

Graduate Students:

D. Cannell, Research Assistant, Physics

N. Clark, Research Assistant, Physics

S. B. Dubin, Research Assistant, Physics

P. Lazay, Research Assistant, Physics

J. Lunacek, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and Engineering

Degrees Granted:

P. D. Lazay, Ph.D., Physics, Feb. 1969
(to Bell Telephone Labs, Holmdel, N. J.)

Sponsorship:

Advanced Research Project Agency, SD-90, DSR 75102

Sloan Fund for Basic Research in the Physical Sciences

U. S. Army Research Office-Durham, DAH CO4-69-C-0034, DSR 71437

CRITICAL PHENOMENA IN SOLIDS AND FLUIDS

1.0 Hypersonic Sound Waves in Ammonium Chloride Near its Order-Disorder Transition

Personnel: G. Benedek; Paul Lazay

Object:

Mr. Lazay has succeeded in measuring the attenuation and the velocity of hypersonic i. e., 10-15 kMC sound waves in crystals of NH_4Cl near its critical point using the technique of high resolution Brillouin scattering of laser light. This research has been completed, his Ph. D. thesis written and accepted by the Physics Department and Dr. Lazay is now working at Bell Telephone Labs in Holmdel, N. J.

2.0 Phonon Lifetimes in Ammonium Chloride

Personnel: G. Benedek; J. H. Lunacek

Object:

Mr. Lunacek has measured, from the widths of the Brillouin components in the scattered light the lifetimes of ~KMHz phonons at fifteen temperatures between - 30°C and room temperature. By changing scattering angles he intends to determine lifetimes of other frequency phonons to determine the characteristic relaxation time of the phonon damping mechanism. Mr. Lunacek and Mr. N. Clark, have recently won the first prize in the Apparatus Competition of the Annual Meeting of the American Association of Physics Teachers.

3.0 Measurements of the Thermal Diffusivity and the Equation of State Near the Critical Point of Sulfur Hexafluoride

Personnel: G. Benedek; J. B. Lastovka

Object:

Dr. Lastovka has measured the intensity of the light scattered from SF_6 near its critical point along the liquid side of the coexistence curve and along an isochore parallel to the critical isochore. He has deduced from the data that the divergence of the isothermal compressibility. The exponent γ' for this divergence is $\gamma'_{liquid} = 1.139 \pm 0.015$. He also finds $\gamma = \gamma'$ from the isochore whose density is $(\rho - \rho_c)/\rho_c \sim 0.4$. By measuring the density of the liquid he finds the exponent for the shape of the coexistence curve is $\beta = 0.33$. By measuring the pressure and density along the critical isotherm he has found $\delta = 4.45 \pm 0.1$. He will carry out similar measurements along isochores closer to the critical density. He will also measure the line width of the scattered light to determine the divergence of the thermal conductivity.

4.0 On the Divergence of the Compressibility and the Ornstein-Zernike Correlation Range in Xenon Near its Critical Point

Personnel: G. Benedek; M. Giglio

Object:

Dr. Giglio has measured the angular dependence of the light scattered from Xenon near its critical point; verified the Ornstein-Zernike theory and determined the temperature dependence of the isothermal compressibility (κ_T); the long range correlation length (ξ) and the direct correlation range (R). The exponents describing the divergences of κ_T and ξ are respectively $\gamma'_{liquid} = 1.228 \pm 0.028$ $\gamma'_{vapor} = 1.244 \pm 0.017$ and $\nu'_{vapor} = 0.57 \pm 0.05$. R is essentially constant at ~ 6 Å. This work has been submitted to Physical Review Letters and Dr. Giglio has returned to the University of Milan.

5.0 Viscosity and Surface Tension at a Gas-Liquid Interface Near the Critical Point

Personnel: G. Benedek; J. Zollweg

Object:

By studying the spectrum of light scattered from "ripplons" at the interface between the gas and liquid phases of a fluid one can measure, without touching the surface, the surface tension and the viscosity of the

fluid. Both these quantities are important indications of the nature of the critical state. Dr. Zollweg is now assembling the equipment necessary for the experiment.

6.0 Hypersonic Sound Velocity and Attenuation in Xenon Near its Critical Point

Personnel: G. Benedek; D. Cannell

Object:

The spectrum of laser light scattered by the adiabatic pressure fluctuations in pure Xenon has been measured along the critical isochore for temperatures ranging from 0.100°C above the critical temperature, T_c, to a temperature of $T_c + 20°C$. The measurements were made using two high resolution spherical Fabry-Perot interferometers in tandem. This was necessary in order to resolve the weak adiabatic portion of the spectrum in the presence of the extremely intense Rayleigh component. For temperatures greater than $T_c + 4°C$ the spectrum was observed to consist of a normal Brillouin doublet and the spectrally unshifted Rayleigh component. In this case the frequency difference between the Rayleigh component and Brillouin component yields the sound velocity while the width of the Brillouin component measures the sound damping. The ratio of the Rayleigh intensity to the Brillouin intensity is equal to (Cp/Cv) the ratio of the specific heats. For temperatures less than $T_c + 4°C$, the spectrum contains in addition, a relatively broad unshifted mode such as has been observed in liquids which undergo a structural relaxation. Mr. Cannell is analyzing the experimental data in terms of the temperature dependence of both the relaxing and non-relaxing portions of the hydrodynamic transport coefficients.

PHYSICAL PROPERTIES OF BIOLOGICAL MACROMOLECULES

7.0 Measurement of Molecular Weight of Bacteriophage Viruses

Personnel: G. Benedek; S. B. Dubin

Object:

Using our measurements of the diffusion constant of the viruses

T_4, T_5, λ and T_7 we have been able to determine for the first time accurate values of the molecular weight of these genetically important bacteriophages.

8.0 Denaturation of Lysozyme

Personnel: G. Benedek; S. B. Dubin

Object:

By measuring the diffusion constant of lysozyme using the techniques of optical mixing spectroscopy we have been able to follow the changes in conformation of this enzyme as a function of the concentration of a denaturant: guanidinium hydrochloride. This work is casting an important light on the precise form of the break-up of this enzyme as it loses its biological function. Mr. Dubin is now writing his Ph. D. thesis.

9.0 Hydrodynamic Properties of Tobacco Mosaic Virus

Personnel: G. Benedek; D. Schaefer

Object:

By measuring the precise shape of the non-Lorentzian spectrum of the light scattered from solutions of tobacco mosaic virus Dr. Schaefer has succeeded in deducing the average translational diffusion constant, and the rotational diffusion constant. A paper describing the experimental measurements and their analysis is now being written.

EXPERIMENTAL INVESTIGATION OF THE BOLTZMANN EQUATION

10. Spectrum of Light Scattered from Pure Xenon Gas and Mixtures of Xenon and Helium

Personnel: G. Benedek; N. Clark

Object:

The theory of transport processes (electrical conductivity, thermal

conductivity, etc.) of solids is based on the Boltzmann equation which was developed for gases. The present investigation is designed to study experimentally the predictions of the Boltzmann equation in gases to establish the range of validity of this fundamental equation. This is done by studying the spectrum of light scattered by density fluctuations in Xenon gas and by mixtures of Xenon and helium. Mr. Clark has constructed for this purpose a uniquely reliable frequency stabilized laser and high resolution Fabry-Perot spectrometer and has now obtained a very substantial number of measurements of the spectrum of the scattered light as a function of gas density. Mr. Clark has completed his analysis of the data and is now in the process of writing his thesis. Mr. Clark was recently awarded, along with Mr. J. Lunacek the first prize in the AAPT Aparatus Competition at the Annual Meeting of the American Physical Society.

Theses:

Paul Lazay, "The Rayleigh-Brillouin Spectrum of Ammonium Chloride," Dec. 1968, Ph. D. Thesis, M. I. T.

Publications:

G. B. Benedek, "Thermal Fluctuations and the Scattering of Light," in Statistical Physics, Phase Transitions and Superfluidity, pg. 1, Ed. by M. Chretien, E. Gross and S. Deser, Published by Gordon and Breach 1968.

G. B. Benedek, "The Spectrum of Light Scattered by Critical Fluctuations," in Light Scattering Spectra of Solids, Ed. by G. B. Wright, Published by Springer-Verlag Inc., N. Y. 1969.

G. B. Benedek, P. Lazay, N. Clark and J. H. Lunacek, "The Rayleigh-Brillouin Spectra of Ammonium Chloride," in Light Scattering Spectra of Solids, Ed. by G. B. Wright, Published by Springer-Verlag, N. Y. 1969.

N. A. Clark and J. H. Lunacek, "A Study of Brownian Motion Using Light Scattering" Am. J. Phys. 37, 853 (1969)

G. B. Benedek, "Optical Mixing Spectroscopy with Applications to Problems in Physics, Chemistry, Biology and Engineering," Polarization, Matter and Radiation, Kastler Jubilee Volume, Published by Presses Universitaire de France Paris 1969.

VI. EXPERIMENTAL STUDIES OF CRITICAL PHENOMENA AND ORDER-DISORDER PHASE TRANSITIONS

Faculty:

J. D. Litster, Assistant Professor, Physics

Graduate Students:

D. D. Berkner, Research Assistant, Physics
J. T. Ho, Research Assistant, Physics
T.R. Steger, N. D. E. A. Fellow, Physics
T. W. Stinson, III, National Science Foundation Fellow, Physics

Senior Students:

R. A. Pearson, Physics
L. L. Perletz, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and Engineering

Personnel who have left:

J. T. Ho (Now Assistant Professor of Physics, University of Pennsylvania, Philadelphia, Pa. 19104)
R. A. Pearson
L. L. Perletz

Degrees Granted:

J. T. Ho, Ph. D., Physics, September 1969
R. A. Pearson, S. B., Physics, June 1969
L. L. Perletz, S. B., Physics, June 1969

Sponsorship:

Advanced Projects Research Agency, SD-90, DSR 75101
National Aeronautics and Space Administration NGR-22-009-182, DSR 76375 (February 1, 1969)

Research Reports

1.0 Magneto-Optical Studies of the Critical Point

Personnel: J. D. Litster; D. D. Berkner, J. T. Ho, T. R. Steger

Object:

To use the rotation of the plane of polarization (Faraday effect) of light transmitted by magnetic solids to study the temperature dependence of the susceptibility and field dependence of the magnetization near the critical point.

Research Report:

1.1 Faraday Rotation in $CrBr_3$

We have completed measurements on $CrBr_3$. A preliminary account of the results has been presented at the 1968 Conference on Magnetism and Magnetic Materials and published in the Journal of Applied Physics. A detailed paper is in preparation.

From this experiment we were able to determine the first equation of state for an insulating ferromagnet in the critical region, and the most precise data for any substance near the critical point.

In collaboration with P. Schofield (Visiting Professor of Physics) we developed a parametric equation of state for the critical region. The resulting equation is mathematically simple, clearly displays the relationship between thermodynamic quantities, and appears to be valid (within experimental errors) for magnetic systems, pure fluids, and binary alloys in the critical region. A preliminary account has been submitted for publication.

A detailed discussion of this experiment and results is to be found in the Ph. D. thesis of J. T. Ho.

1.2 Faraday Rotation in YIG

We have completed a series of preliminary measurements on yttrium iron garnet using Faraday rotation at 1.15μ. We found the reproducibility of our measurements to be unsatisfactory and traced this to temperature gradients in our oven. The oven is being redesigned and

we shall then determine the critical behavior of YIG.

1.3 Critical Properties of EuS

With a simple cubic structure and no anisotropy, EuS should be rather well described by the Heisenberg model. We are therefore greatly interested in studying its critical properties. We have observed a large Faraday effect in one sample and are currently preparing a higher quality sample and calibrating our thermometer prior to making accurate measurements on this material.

2.0 Phase Transitions in Liquid Crystals

Personnel: J. D. Litster; T. W. Stinson

Object:

To study the nature of order-disorder transitions in liquid crystals and elucidate the similarities and differences between liquid crystals and other materials exhibiting critical behavior.

Research Report:

We have used a high resolution spherical Fabry-Perot interferometer and a single frequency laser to measure the time dependence of local fluctuations in order in the isotropic phase of a nematic liquid crystal. Our experiment shows that ordering in nematic liquid crystals has much in common with order-disorder transitions in other systems. We find a critical slowing of the fluctuations analogous to the critical slowing of spin fluctuations in a ferromagnet. The fluctuations relax exponentially with a single relaxation time τ. Over two decades of τ we find that $\tau \sim (T - T_c^*)^{-\gamma}$ with $\gamma \simeq 4/3$ and T_c^* slightly below the temperature at which the first order phase transition occurs.

We are extending our measurements to learn the effects of electric and magnetic fields and compare the behavior of various liquid crystalline materials.

Theses:

J. T. Ho, "Faraday Rotation Near the Ferromagnetic Critical Temperature," Ph. D., Physics

R. A. Pearson, "Frequency Stabilization of an Argon Ion Laser," S. B., Physics

L. L. Perletz, "A Temperature Control and Stabilization System for the Study of Low Temperature Critical Phenomena by Optical Methods," S. B., Physics

Publications:

John T. Ho and J. D. Litster, "Divergences of the Magnetic Properties of $CrBr_3$ Near the Critical Point," J. Appl. Phys. 40, 1270 (1969).

John T. Ho and J. D. Litster, "Magnetic Equation of State of $CrBr_3$ Near the Critical Point," Phys. Rev. Letters 22, 603 (1969).

P. Schofield, "Parametric Representation of the Equation of State Near a Critical Point," Phys. Rev. Letters 22, 606 (1969).

P. Schofield, J. D. Litster, and John T. Ho, "Correlation Between Critical Coefficients and Experiments," submitted to Phys. Rev. Letters.

J. D. Litster and Thomas W. Stinson, III, "Critical Slowing of Fluctuations in a Nematic Liquid Crystal," J. Appl. Phys., to be published (as proceedings of 1969 Conference on Magnetism and Magnetic Materials).

VII. THE DYNAMICS OF QUANTUM FLUIDS

Faculty:

T. J. Greytak, Assistant Professor, Physics

Graduate Students:

R. Benjamin, Research Assistant, Physics
E. Grace, Graduate Student, Physics
D. Rockwell, Graduate Student, Physics
R. St. Peters, N. S. F. Predoctoral Fellow, Physics
R. Woerner, Graduate Student, Physics
J. Yan, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and Engineering

Personnel who have left:

R. St. Peters, N. S. F. Predoctoral Fellow, Physics (Now at G. E. Research Laboratory, Schenectady, N. Y.)

Degrees Granted:

R. St. Peters, Ph. D., Physics, September 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75103

Research Reports

1.0 Rotons in Liquid Helium

Personnel: T. J. Greytak; J. Yan, R. Woerner

Research Report:

We have measured the spectrum, intensity, and polarization of light Raman scattered from rotons and higher energy elementary excitations in the superfluid phase of pure He^4. We have determined, from the temperature dependence of the spectrum, roton energies and

lifetimes from 1.16 ^{o}K to 1.9 ^{o}K. Our measurements of intensity and polarization have been used to test several theories of the coupling between light and elementary excitations in solid and liquid helium. We are extending these measurements to dilute solutions of He^3 in He^4 and to pure He^3. We are developing a Fabry-Perot spectrometer to be used in measuring roton lifetimes at temperatures near 1 ^{o}K.

2.0 Thermal Sound Waves in Superfluid Helium

Personnel: T. J. Greytak; R. St. Peters

Research Report:

We have measured the velocity and amplitude absorption coefficient of thermally-driven first sound in liquid He^4 under its saturated vapor pressure between 1.25 ^{o}K and the lambda point. The sound wave vector was fixed at 2.0339×10^5 cm^{-1}, corresponding to a frequency varying from 768 MHz at 1.245 ^{o}K to 709 MHz at 2.168 ^{o}K. The velocity data are accurate to better than ± 0.1% while the absorption uncertainty is ± 10%. The data below the lambda region agree well with the Khalatnikov and Chernikova theory of sound propagation in He^4 for the temperature and frequency intervals in which the equations of the theory have been solved. Near the lambda point the data cannot be explained by the single relaxation theory of Landau and Khalatnikov. These measurements are being extended to dilute solutions of He^3 in He^4 and pure He^3. A feature of these experiments will be the ability of light scattering to be used as a probe of second sound, a propagating temperature waves, in the superfluid phase of these mixtures.

3.0 Concentration Fluctuations and Second Sound Near the Phase Separation Point of He^3 - He^4 Mixtures

Personnel: T. J. Greytak; R. Benjamin, D. Rockwell

Research Report:

Existing high power single mode lasers and high resolution Spherical Fabry-Perot interferometers will be used in a study of the dynamics of thermodynamic fluctuations near the phase separation point in isotopic solutions of helium. We are having a He^3 cryostate built which will allow

this and other light scattering studies of liquid helium to be carried out at temperatures as low as 0.3 ^{o}K.

4.0 Dynamics of Polyatomic Gases

Personnel: T. J. Greytak; E. Grace

Research Report:

We are setting up a high resolution, high sensitivity light scattering system to extend our previous measurements of the density fluctuation spectrum of monatomic gases to the study of polyatomic gases. The spectra of monatomic gases have been successfully predicted by the kinetic theory of gases and the Boltzmann equation. A recent extention of the Boltzmann equation to polyatomic gases shows that additional features should occur in the spectrum of density fluctuations. We are in an excellent position to investigate these additional features experimentally by light scattering measurements.

Theses:

R. St. Peters, "Brillouin Scattering in Liquid Helium," Ph. D. Physics, August 1969

Publications:

T. J. Greytak and James Yan, "Light Scattering from Rotons in Liquid Helium," Phys. Rev. Lett. 22, 987 (1969)

VIII. COOPERATIVE PHENOMENA, STATISTICAL MECHANICS, AND SOLID STATE PHYSICS

Faculty:

H. E. Stanley, Assistant Professor, Physics

Research Staff:

M. H. Lee, DSR Staff, Physics

Graduate Students:

J. A. Janzen, USAF Fellow, Physics
K. Matsuno, Research Assistant, Physics
S. Miloševič, Research Assistant, Physics
G. Paul, Teaching Fellow, Physics
H. I. Botman, Senior Student, Physics
M. L. Jennings, Senior Student, Physics
S. H. Kinney, Jr., Senior Student, Physics
R. M. Lucash, Senior Student, Physics
D. L. Njus, Senior Student, Physics
C. C. Lo, Senior Student, Physics

Support Staff:

Susan Leonard, Secretary, Center for Materials Science and Engineering

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 71621

Research Report

1.0 Methods for Obtaining Numerical Predictions for Comparison with Experimental Measurements in the Critical Region of Magnets and Fluids

There has been considerable activity in recent years concerning both experimental and theoretical aspects of critical phenomena (i. e. phenomena associated with phase transitions). On the experimental side, extremely accurate measurements have been made for temperatures exceedingly close to the critical temperature T_c. Therefore what one wishes to predict theoretically are the behaviors of the various thermodynamic quantities in the immediate neighborhood of T_c, and these behaviors are generally characterized by

a set of "critical exponents". It is unlikely, however, that even the simplest realistic models of liquid-gas and magnetic phase transitions (e.g. the Ising and Heisenberg models, respectively) will be solved exactly for three-dimensional systems in the immediate future. Hence if one wishes to obtain the specific predictions of a theoretical model, one must resort to approximation techniques. Probably the most accurate of these is the method of high-temperature series expansions. There are many theoretical models for which numerical predictions would aid greatly in interpreting recent experimental results. We have developed two new techniques which permit obtaining critical behavior predictions for a wide variety of theoretical models which were not previously tractable. The first of these techniques concerns the actual calculation of the high-temperature expansions, and the second concerns the analysis of the series.

1.1 New Method for Developing High-Temperature Expansions

Very recently we have discovered a new method by which we can calculate high-temperature expansions with at least an order of magnitude less labor than was required previously. This method utilizes certain topological relations to obtain a generalized diagrammatic representation suitable for calculating all the thermodynamic quantities of interest. We are presently developing new and better expansions using this method; thus far we have already obtained several new results. One such result is that the specific heat exponent for the Heisenberg model has a cusp singularity, which is consistent with recent experimental measurements on the "Heisenberg ferromagnet" EuS.

1.2 New Transformation Method to Analyze Series Expansions

We have recently discovered a method which is capable of analyzing certain series expansions whose coefficients vary irregularly and which heretofore could not be analyzed accurately. This method exploits the concept of the "Euler transformation" to shift the non-physical poles to a location further from the origin in the complex temperature plane.

2.0 Critical Point Exponents

2.1 Susceptibility Exponent γ (S) for $S > 1/2$

We considered the question of the possible dependence of the susceptibility exponent γ (S) upon spin quantum number S for the 3-dimensional Heisenberg model. We argued that $\gamma(S) = 1.38 \pm 0.01$ for all S greater than 1/2. For $S = 1/2$, the susceptibility series behaves too irregularly for any conclusions

to be drawn using conventional series methods.

2.2 Critical Exponents for the $S = 1/2$ Heisenberg Ferromagnet

Baker et. al. have recently argued that for the $S = 1/2$ Heisenberg ferromagnet, the susceptibility and gap in exponents have the values $\gamma = 1.43 \pm 0.01$ and $2\Delta = 3.63 \pm 0.03$ respectively. We find that the high temperature series expansions can be better analyzed using the Euler transformation method, and we thereby obtain the more accurate values $\gamma = 1.36 \pm 0.02$ and $2\Delta = 3.48 \pm 0.05$ To the extent that the homogeneity or scaling arguments are valid, a knowledge of the two exponents γ and Δ is sufficient to obtain all other exponents.

2.3 Critical Exponents for the Ising, XY, and Heisenberg Models on the Spinel Lattice

There is considerable evidence to support the hypothesis that critical point exponents do not depend upon the type of lattice, but only upon the lattice dimensionality. However this evidence depends largely on studies of particularly simple lattices such as the simple cubic, body centered cubic, and face centered cubic lattices. The spinal lattice, on the other hand, has a rather more complex structure; moreover, certain insulating materials have this structure. Due to the irregular nature of the coefficients in the high-temperature expansions, it was not previously possible to obtain information concerning the critical point exponents for the spinel lattice. However by applying the Euler transformation, we have recently obtained fairly accurate estimates of the critical indices, and we find that they are <u>different</u> from those of the simpler lattices.

2.4 Critical Point Exponents for the Ising, Heisenberg, and Spherical Models as a Function of Lattice Dimensionality

The lattice dimensionality d enters into some of the relationships among the various critical point exponents which are predicted by the static scaling hypothesis. For this and other reasons, we have calculated high-temperature expansions for the susceptibility, specific heat, second moment, and field dependent free energy for a general d-dimensional lattice and thereby we have determined, respectively, the exponents $\gamma(d)$, $\alpha(d)$, $\nu(d)$, and $\Delta(d)$ as functions of d. We find rather striking evidence that the exponents studied depend monotonically upon d, and that they approach their respective mean field values in the limit $d \to \infty$, although neither of these results has been proved rigor-

ously. Moreover, we advance arguments supporting the possibility that the mean field values of the exponents are obtained for all $d > 3$.

3.0 Phase Transitions in Planar Materials

3.1 The Staggered Susceptibility of the Planar Antiferromagnet

It has commonly been supposed that the two-dimensional Heisenberg model with nearest-neighbor ferromagnetic interactions will not undergo a phase transition. Over a year ago we presented evidence from high-temperature expansions suggesting the contrary. This theoretical possibility has derived significant experimental support from recent work at Bell Telephone Laboratories (Wertheim, et. al.), Brookhaven Laboratory (Birgeneau, Shirane, et. al.), and the University of Amsterdam (Miedema, et. al.) on materials with the K_2NiF_4 structure in which the inter-planar interactions are as much as 10^5 times weaker than the intra-planar interactions. However the experimental materials have an antiferromagnetic exchange interaction, whereas the original theoretical prediction was based upon a model with a ferromagnetic interaction. Hence we have recently carried out an analogous treatment for the staggered susceptibility of a Heisenberg antiferromagnet. The evidence favoring a divergent staggered susceptibility is found to be essentially as strong as that presented earlier in support of a divergent susceptibility for the ferromagnet. Thus recent work on the "planar antiferromagnets" would appear to be strongly supported by the series expansion theory.

3.2 The Susceptibility for $S = 1/2$

The argument for a phase transition in two-dimensional materials which was proposed by Stanley and Kaplan is based upon the behavior of the high-temperature series for the susceptibility for $S > 1/2$. For the $S = 1/2$ case, the susceptibility series behaves so irregularly that it is difficult to extract any information. We have recently discovered a method, the Euler transformation, which is capable of analyzing certain high-temperature series expansions with irregularly-varying coefficients. This method is applied to the series for $S = 1/2$. Our results provide evidence for a phase transition of the Stanley-Kaplan type. The critical temperature which we predict for the square lattice agrees well with the measured values recently given by deJongh et. al. for materials with the K_2NiF_4 structure.

4.0 Influence on Critical Properties of Exchange Interactions other than Nearest-Neighbor

Almost all calculations on model systems make the assumption that the exchange interaction extends in range only to the nearest neighbor atoms in the lattice. However most real magnetic materials have exchange interactions which are of longer range. Therefore to afford more realistic comparison with experiment, we are extending several calculations for nearest-neighbor systems to include further neighbor forces.

5.0 Phase Transitions in Non-Ideal Bose Systems

5.1 The XY Model of a Quantum Lattice Fluid

Matsuda and Matsubara's lattice model for liquid helium reduces to the XY model for hard-core intermolecular interactions. In collaboration with Professor D. D. Betts, we have calculated critical properties for the XY model using series expansion methods. We are presently studying the low-temperature behavior and, in particular, looking at the case of 2-dimensional lattices.

5.2 Theory of Correlation and Critical Point Scattering in the Vaks-Larkin Lattice Model of Helium

Another lattice model for the λ transition is the Vaks-Larkin or plane rotator model. We have calculated the correlation function exponents for this model. In particular, we find that the asymptotic decay of correlations at the critical temperature is $R^{-1+\eta}$ with η very slightly greater than the value (zero) predicted by the standard Ornstein-Zernike theory.

5.3 Critical Properties of Non-Ideal Bose Systems

Recently Professors M. Luban and M. Revzen have obtained certain critical properties of an ideal Bose gas by relating the divergence of the constant-pressure specific heat and the isothermal compressibility to the onset of off-diagonal long range order. We have adopted this approach in order to treat the more interesting non-ideal gas models of Bogoliubov.

6.0 Thermodynamic Fluctuations in Ferromagnets

Thermodynamic fluctuations in a statistical system have been investigated.

The statistical system is assumed to be divided into two subsystems A and B, each of which might not be in equilibrium itself. The resultant system A plus B is now assumed to be in equilibrium. Although each subsystem A and B can fluctuate independently, another type of fluctuation is expected due to the interaction between A and B, in each of which the rate of entropy production is not zero. Fluctuations in the rate of entropy production can give rise to a time-dependent fluctuation of statistical or thermodynamic quantities. When the relaxation times of each subsystem are τ_A and τ_B, and further $\tau_A \gg \tau_B$ is satisfied, the present fluctuation due to the spontaneous variation of the rate of entropy production will become dominant for the relaxation phenomena whose relaxation time t satisfies the condition $\tau_A \gg t \gg \tau_B$. Near the Curie point T_c of ferromagnets, it is possible to expect the coexistence of locally ordered and disordered states. The application of the present theory to critical fluctuations near T_c has been studied.

7.0 Research on the Spherical Model of Magnetism

7.1 Spherical Model as the Limit of Infinite Spin Dimensionality

The spherical model is important because it is essentially the only exactly soluble model of a 3-dimensional system which is non-trivial. We have recently shown that the spherical model is equivalent to the $D = \infty$ limit of the Hamiltonian $H^{(D)} = -J\Sigma_{<i,j>} \underset{\sim}{S}_i^{(D)} \cdot \underset{\sim}{S}_j^{(D)}$, where $\underset{\sim}{S}_i^{(D)}$ are isotropically interacting D-dimensional classical spins. This result has led to a new concept of the spherical model as an "anchor point" in a hierarchy that includes the Ising model (D=1), the Vaks-Larkin model (D=2), and the Heisenberg model (D=3). In particular, we have conjectured on the basis of numerical evidence, that the various critical properties of $H^{(D)}$ are monotonic functions of spin dimensionality D; this would imply that although the spherical model was previously regarded as a soluble approximation to the Ising model, it is in fact a much better approximation to the Heisenberg model.

7.2 Spherical Model as an "Anchor Point" with which to Judge Approximation Procedures

A knowledge of the properties of the model Hamiltonian $H^{(D)}$ provides one with an "anchor point", since $H^{(D)}$ is not soluble for other values of D. For example, we have recently calculated 100 terms in the high-temperature expansions of the specific heat and susceptibility of the spherical model for a general d-dimensional hypercubical lattice. The 100 terms in the spherical

model series provide an ideal "fruitfly" on which to test various extrapolation procedures; thus far we have discovered a significant flaw in the Padé approximant procedure using this concept.

8.0 Exact Solution for a Linear Chain of Isotropically Interacting Classical Spins of Arbitrary Dimensionality

The isotropic Hamiltonian $H^{(D)} = -J\Sigma_{i=1}^{N-1} \underset{\sim}{S}_i \cdot \underset{\sim}{S}_{i+1}$ is considered for an open linear chain of D-dimensional classical spins $\underset{\sim}{S}_i$. We have solved this system exactly for all the thermodynamic properties both for ferromagnetic ($J>0$) and for antiferromagnetic ($J<0$) interactions. We find that all of the properties vary monotonically with D; e.g., the "short range order" decreases monotonically with increasing spin dimensionality.

9.0 Eigenvalue Degeneracy as a Possible "Mathematical Mechanism" for Phase Transitions

Some years ago Ashkin and Lamb noted that the phase transition in the two-dimensional Ising model with nearest-neighbor interaction was characterized mathematically by an asymptotic degeneracy of the largest eigenvalue of a linear operator. More recently Kac and Thompson showed this eigenvalue degeneracy also characterized the phase transition in the Kac model (with weak, long-range forces), suggesting that this "mathematical mechanism" is not restricted to systems with short-range forces. However both the Kac model and the Ising model consider the "spins" to be one-dimensional unit vectors assuming only the discrete values +1 and -1. We are therefore led to consider the nature of the phase transition in one of the few exactly-soluble models in which the spins can assume an entire continuum of orientations--the linear chain of classical spins of arbitrary spin dimensionality interacting isotropically through the Hamiltonian $H^{(D)} = \Sigma_{i=1}^{N} J_{i,i+1} \underset{\sim}{S}_i^{(D)} \cdot \underset{\sim}{S}_{i+1}^{(D)}$, where the exchange constants $J_{i,i+1}$ are arbitrary numbers. We find for all spin dimensionalities D that the two-spin correlation function may be expressed as $\rho_N(r) = (\lambda_1/\lambda_0)^r$, where λ_0 and λ_1 are the largest and next-largest eigenvalues of a certain linear operator. Thus the onset of long-range order, $\lim_{r\to\infty} \rho_N(r) \neq 0$, is characterized by the degeneracy of λ_0 and λ_1.

10.0 A New Cluster Approximation in which the Basic Cluster is an Entire "Chain" of Spins

There exist magnetic materials in which the magnetic ions may be con-

sidered to form "linear chains" such that interactions between spins within a chain are appreciably stronger than interactions between spins belonging to different chains. Hence, we have studied a model in which the interactions are treated exactly and the interchain interactions are treated approximately (say, using the molecular field approximation). Preliminary calculations using the classical Heisenberg model suggest that this is a realistic model for temperature not too near T_c.

11.0 New Expansion of the Spin Correlation Function

The practical advantages of carrying out a high-temperature expansion of the spin correlation function are yet to be exploited. In particular, some preliminary calculations indicate that this expansion may be used to predict, rather accurately, observed neutron scattering cross sections.

12.0 Liquid Helium^4

12.1 The Jastrow Theory and the Ground State

Most of the theories of liquid helium are not capable of providing a correct description of the ground state. Several years ago Jastrow devised a method which, although it possesses certain advantages over the model theories of Bogoliubov and others, has a serious drawback in its mathematical complexity (particularly when it deals with the pair distribution function). We have devised a method to solve an integral equation for the pair distribution function and we have thereby obtained many of the ground state properties of liquid helium. In particular, the speed of first sound agrees well with experiments.

12.2 Finite Temperature Theory

We are extending our T=0 results to non-zero temperature in order to examine the temperature dependence of the pair distribution function. Our analytic solution for the integral equation for the pair distribution function has led to a method of deducing certain critical properties. We have thereby obtained, for example, the asymptotic form of the pair correlation function.

12.3 Generalized Bose Condensation and Symmetry-Breaking Ground State

It is known that pair product functions, such as the Jastrow function,

predict an incorrect long wavelength behavior for the liquid structure factor S(k). The modification needed in the pair product functions which will give the correct small-k behavior for S(k) appears to be not higher correlations, but uncorrelated single particle functions coupled to the pair product function. Also work on models of liquid helium shows evidence that, with attractive interactions, the usual notion of Bose condensation is not valid. An investigation is underway to see whether these models with attractive interactions and generalized Bose condensation can be further exploited and whether the logarithmic specific heat singularity observed in liquid helium can be explained in terms of these models.

12.4 The Structure Factor of Liquid Helium[4]

Experimental values of the structure factor S(k) of liquid helium deviate substantially for small k values from the Feynman prediction. We have found that the discrepancy is due to a certain invalid assumption in interpreting experimental scattering data. Moreover, our analysis predicts that at low temperatures gaseous helium is not an ideal gas as previously assumed; this prediction has recently been confirmed by experiments.

12.5 Integral Equations and the Pair Distribution Function

We have recently shown that the pair distribution function can be solved using hypernetted chain integral equations. The method of iteration turns out to have an interesting relation to the Green's function formulation of many-body problems. By exploiting this correspondence, certain analytic properties of the pair distribution function are obtained. The knowledge of the analytic structure has enabled us to obtain the density dependence of the distribution function. Our results show that as the density increases, particles tend to get packed in a certain ordered fashion, exhibiting certain similarities to solid helium. Following some earlier work of deBoer, we are at present extending our results to study the compressibility of liquid helium near the critical density.

13.0 Many Body Problems

13.1 Interacting Many-Fermion Systems

Recently we have shown that Tomonaga's work on interacting many-fermion systems is more general than previously recognized. Since the Tomonaga model is exactly soluble for any interactions, it may serve as a useful model for liquid helium[3], particularly for studying features of helium[3] such as freezing or as a test of the general stability criteria for Fermi liquids.

13.2 Theory of Quantum Liquids

Bogoliubov, Born, and Green have suggested that many interesting features such as the onset of long-range order may be indicated by the change in the analytic character of the distribution function. We have found a way of extending their suggestion to quantum fluids by using a certain formal correspondence principle.

13.3 Cluster Expansions for Many-Boson Systems

We have recently shown that the pair distribution function of quantum fluids can be obtained by modifying slightly the methods developed for classical fluids. If the N-body wavefunction contains only the 2-body correlations, one can directly use the hypernetted chain integral equations. If the N-body wavefunction contains explicitly one and two-body correlations, then one encounters a quantum analog of the Mayer cluster expansion. We have developed a diagrammatic method of evaluating the cluster expansion by taking advantage of Kubo's cumulants.

13.4 Analyticity and the Spin Pair Correlation Function

In the study of the magnetic susceptibility or the spin pair correlation function, there emerges a good deal of information regarding the analytic character of the function. This is particularly true of Padé approximant analysis of the power series expansions for the susceptibility. One obtains, for example, various singularities of the susceptibility, of which, however, only the value for the physical pole is generally noticed and nonphysical poles are usually disregarded. Analysis of the power series for the susceptibility by the Euler transformation method shows a certain relationship between the physical and nonphysical poles quite reminiscent of the dispersion relation for particle scattering amplitudes. In particular there apprears to be some formal correspondence between the bound state and the physical pole (the critical point).

14.0 Electronic Charge and Momentum Distributions in Crystals

In collaboration with researchers at the M.I.T. Lincoln Laboratory, we have carried out two research projects in this area.

14.1 Bloch Sums of Localized Orbitals in One Dimension: Charge and Momentum Densities

Bloch functions and the charge and momentum densities for partially-filled bands of Bloch functions have been examined. The Bloch functions are represented as linear combinations (Bloch sums) of localized orbitals. A

detailed discussion has been given for two one-dimensional models; for one the localized orbital is an exponential and for the other it is a Gaussian. Calculations are largely analytical for these models. The results for the two models agree qualitatively in some respects, and show clearly the effects of orbital overlap; the behavior in the limit of small and large overlap is particularly instructive. For the two models the charge density of a Bloch function is found to become more localized as the wave vector k increases in the Brillouin zone, and the total charge density for a filled band is never less localized than that obtained by superposing the charge densities of the corresponding localized orbitals. The x-ray intensity oscillates for the Gaussian model but not for the exponential. In the limit of large overlap, the Bloch functions approach plane waves for the Gaussian model, but not for the exponential. For a filled band the momentum density is for both models much more sensitive to overlap than is the charge density.

14.2 Effect of Orbital Overlap on Charge Densities in Three-Dimensional Crystals

The Heitler-London approximation to the ground state of a crystal composed of closed-shell ions (e.g., MgO, LiH) is $\psi = \mathcal{A}\Pi_\alpha D_\alpha$; where D_α is a Slater determinant for ion α. The customarily neglected effects of the antisymmetrizing operator $\mathcal{A}$ may well be important in interpreting measured charge densities. An effect of this "determinantal overlap" on the x-ray structure factor $f(q)$ can be illustrated for LiH, for example, by approximating the Li^+ and H^- 1-electron wavefunctions by exponential 1s orbitals. We have calculated $f(q)$ for the rocksalt structure with 2 electrons per site, approximating the orbitals using Gaussian rather than exponential orbitals. We find that the ratio of $f(q)$ to the "conventional" (no overlap) structure factor, $f_c(q)$ has a characteristic variation with q which is quite similar to that reported for an experiment on MgO. Moreover, a crude estimate of the actual magnitude of this "overlap effect" for MgO shows that $f(q)$ can depart from $f_c(q)$ by roughly 5%, so that the effect should be experimentally significant.

15.0 Application of Modern Physical Methods to Biological and Medical Problems

15.1 Raman Spectra of Biological Molecules

In collaboration with researchers at the M.I.T. Lincoln Laboratory,

we have initiated an effort to formulate physical problems of biological and medical interest. In particular, we have begun a study of the Raman spectra of biological molecules, using equipment previously developed for solid state investigations. Raman spectroscopy serves to complement the more traditional technique of infrared spectroscopy in that one can avoid problems associated with various absorption bands (such as those of H_2O).

15.2 Cooperative Phenomena in Biological Membrane Systems

We have begun to formulate quantitative models of biological membrane systems. We are finding strong analogies between these models and lattice systems which display cooperative phenomena. Therefore we are attempting to provide a quantitative explanation of "cooperative phenomena" in biological membranes by adapting certain methods which have been extremely successful in describing the lattice systems.

15.3 The Unwinding Phase Transition of DNA

Double-stranded DNA molecules suddenly "unwind" upon heating them to a temperature "T_c". This phase transition has some features in common with certain one-dimensional cooperative systems. We are attempting to formulate a precise model which describes this transition.

15.4 The Molecular Mechanism of Photosynthesis

The photosynthetic process probably involves the "hopping" from site to site of a so-called exciton. This physical process has a mathematical analog in a certain kind of random walk. Therefore we have begun an intense study of the relation of random walk problems to photosynthesis.

16.0 Computer Enhancement of Air Traffic Control Data

In recent years sophisticated data processing techniques have been developed for the selection and augmentation of electronic sensor data. Concurrently, the physical causes of radar data positioning error and background noise have become well understood. With further efforts, the above two technologies can be applied to the contemporary problem of air traffic control. With the ever greater crowding of the world's airways, the credibility of air control radar data should not be in doubt. The application of these further efforts will be made from two viewpoints. First, the effectiveness of apply-

ing data enhancement techniques to returns from existing equipment will be evaluated. It is possible that careful real time computer processing alone can significantly offset errors caused by atmospheric conditions and degraded equipment. Second, the advantages of applying modern technology to the problem of aircraft position sensing will be considered. Several new systems now appear applicable and are being studied: A. HOLOGRAPHIC RADAR - By constructing large phase sensitive dipole arrays it is possible to obtain three dimensional data of very high resolution. Although the cost of these units is very high, they may be justified for computer controlled landing patters. B. REVERSE DATA LINK - By equipping the aircraft with high resolution navigational equipment and having it transmit this data to the air control center, commercial aircraft could be closely controlled in areas of poor radar coverage. C. IR AIRCRAFT TRACKING - t may be more economical to observe aircraft from space than to build more stationary or airborne radar units. Jet aircraft emit large amounts of infra-red radiation, some of which could be detected outside the atmosphere.

Publications

H. E. Stanley, Critical Phenomena: An Introduction to Phase Transitions, to be published by W. A. Benjamin, Inc. as a book in the series "Frontiers in Physics"

H. E. Stanley, Readings in Critical Phenomena, a companion volume to the above.

H. E. Stanley, Critical Phenomena in Heisenberg Models of Magnetism, Chapter 14 of Solid State Physics, Nuclear Physics, and Particle Physics, I. Saavedra, Ed. (W. A. Benjamin, Inc. New York, 1969)

H. E. Stanley, "Spherical Model as the Limit of Infinite Spin Dimensionality" Phys. Rev. 176, 718 (1969)

H. E. Stanley, "Exact Solution for Linear Chain of Isotropically-Interacting Classical Spins of Arbitrary Dimensionality", Phys. Rev. 179, 570 (1969)

H. E. Stanley, "Critical Indices for a System of Spins of Arbitrary Dimensionality Situated on a Lattice of Arbitrary Dimensionality", J. Appl. Phys. 40, 1272 (1969)

H. E. Stanley, "Some Critical Properties of Quantum-Mechanical Heisenberg Ferro- and Antiferromagnets", J. Appl. Phys. 40, 1546 (1969)

H. E. Stanley, "Relation among Ising, Heisenberg, and Spherical Models: Properties of Isotropically-Interacting Spins of Arbitrary Dimensionality", J. Phys. Soc. Japan 26, 102 (1969) (Proc. IUPAP International Conference on Statistical Mechanics, Kyoto, Japan)

H. E. Stanley, K. Matsuno, and S. Milošević, "Eigenvalue Degeneracy as a Possible Mathematical Mechanism for Phase Transitions", J. Appl. Phys. (in press).

J. Hanus, T. A. Kaplan, W. H. Kleiner, and H. E. Stanley, "Bloch Sums of Localized Orbitals in One Dimension: Charge and Momentum Densities" Phys. Rev. (in press).

K. Matsuno, "Thermodynamic Fluctuations in Ferromagnets", submitted for publication

M. H. Lee and D. D. Betts, "Critical Properties of the XY Model", Phys. Rev. Letters 20, 1507 (1968)

M. H. Lee, "The Pair Distribution Function of a Quantum Fluid, Physica 43, (1969)

M. H. Lee, "High Temperature Expansion of the Spin 1/2 XY Model", J. Math. Phys. (in press).

M. H. Lee, Cluster Expansion in a Bose Fluid," J. Math. Phys. (in press)

M. H. Lee, D. D. Betts, and C. J. Elliot, "Partition Function and Specific Heat of the XY Model on a FCC Lattice", Phys. Letters 29A, 150 (1969)

M. H. Lee, "The Structure Factor of Liquid Helium^4": The Apparent Discrepancy Between Theory and Experiment," Phys. Rev. Letters 23, 370 (1969)

M. H. Lee and M. Luban, "Ground State of Liquid Helium^4 : I. Correlations", Phys. Rev. submitted.

M. H. Lee, D. D. Betts and C. J. Elliot, "Evidence Favoring a Phase Transition for some 2-Dimensional Models", Phys. Rev. Letters, submitted.

M. H. Lee, "On the Spin 1/2 Heisenberg Ferromagnet for Cubic Lattices" Phys. Rev. Letters

M. H. Lee, "The XY and Heisenberg Ferromagnets on the B-Site Spinel Lattice" Phys. Rev. Letters.

M. H. Lee and M. Luban, "Ground State of Liquid Helium^4: II Energy" Phys. Rev., submitted.

IX. LOW TEMPERATURE PHYSICS - Ultrasonic Study of the He^4 Critical Point.

Staff:

Dr. Richard C. Williamson, Visiting Scientist, Center for Materials

Sponsorship: National Aeronautics and Space Administration - Electronics Research Center

Research Report:

Measurements of the velocity and attenuation of 1 MHz sound waves have been made along a series of isotherms near the critical point of He^4. Data along isotherms which cross the vapor pressure curve below T_C indicate that the sound velocity in the saturated gas is higher than the velocity in the liquid for temperatures close to T_c. This behavior is similar to that observed in several other substances.

Sound attenuation rises to very high values in a small region of pressure close to P_c. The apparent divergence of the sound attenuation as a function of reduced pressure at $T = T_c$ can be characterized by an exponent of 1.1 ± 0.3 which is consistent with the value of 6/5 which is predicted by simple dynamic scaling law arguments. In the region of high attenuation, the variation of the sound velocity departs from the logarithmic form observed earlier by Williamson and Chase for pressures farther from P_c.

Because the sound attenuation is so high near the critical point, we have developed ultrasonic techniques which significantly extend our experiment range by enhancing the signal-to-noise ratio and reducing stray coherent signals. Attenuations of several hundred d.b. per centimeter have been measured using these techniques. The attenuation rises so abruptly in such a very small region of pressure close to P_c, that it is difficult to ascertain the exponents describing the variation of sound velocity and attenuation. To better resolve the region close to the critical point, a new apparatus has been constructed which uses density instead of pressure as an independent variable. With this apparatus, measurements along isochores are now possible.

Publications:

R. C. Williamson and C. E. Chase, "Velocity of Sound at 1 MHz near the He^4 Critical Point", Phys. Rev. 176, 285 (1969).

R. C. Williamson, "Measurement of the Velocity and Attenuation of Ultrasonic Pulses in the Presence of Noise", Rev. Sci. Instr. 40, 666 (1969).

R. C. Williamson, "Echo Phase-Comparison Technique and Measurement of Sound Velocity in Water", J. Acoust. Soc. Am. 45, 1251 (1969).

R. C. Williamson and Don Eden, "Coherent Detection Technique for Variable Path Length Measurements of Ultrasonic Pulses", submitted to J. Acoust. Soc. Am.

X. SEMICONDUCTORS AND INFRARED SPECTROSCOPY

Personnel:

R. A. Smith, Professor, Physics
Dr. S. Zwerdling, Research Staff
J. P. Theriault, Engineering Assistant
F. Q. Yee, Engineering Assistant

1.0 Research Report:

This research Program, described in the Annual Report for 1967-68, was completed in the summer of 1968 when the senior members of the staff involved left the Institute for other employment. The results of the research have now been fully published as indicated below.

1.1 Spectroscopy in the Very-far Infrared

A full report of the theory and operation of the fast low-temperature germanium bolometer developed in this program has been published:

S. Zwerdling, R. A. Smith, and J. P. Theriault, "A Fast, High-responsivity Bolometer Detector For The Very-far Infrared, "Infrared Physics, 8, 271 (1968).

S. Zwerdling, J. P. Theriault and H. S. Reichard, "A Far Infrared Bolometer Pre-Amplifier with Low-Noise Performance at High Impedance," Infrared Physics, 8, 135 (1968).

"The Low-temperature Transmittance of Two Far Infrared LWP Filters", Appld. Optics, 7, 209 (1968)

1.2 Far Infrared Absorption in Semiconductors

This research was presented at the Ninth International Conference on the Physics of Semiconductors, Moscow, and published in the Proceedings of the Academy of Sciences of the USSR:

R. A. Smith, S. Zwerdling, S. N. Dermatis and J. P. Theriault, "Absorption of Compensated Germanium in the Very-far Infrared," Proceedings of the Ninth International Conference on the Physics of Semiconductors, p. 149(1968).

XI. ORDER-DISORDER PHENOMENA

Faculty:

C. W. Garland, Professor, Chemistry

Research Staff:

Dr. E. Litov, Research Associate, Chemistry

Graduate Students:

A. Bonilla, Commonwealth of Puerto Rico Fellow, Chemistry
D. Eden, Research Assistant, Chemistry
P. E. Mueller, Research Assistant, Chemistry
B. B. Weiner, Research Assistant, Chemistry

Support Staff:

Janet Pollock, Secretary, Chemistry

Personnel who have left:

P. E. Mueller (Now at Bell Telephone Laboratories, Allentown, Pa.)

Degrees Granted:

P. E. Mueller, Ph.D., Chemistry, June 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75104
National Science Foundation Grant, GP-7738, DSR 70706
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

Personnel: C. W. Garland; E. Litov; D. Eden, P. Mueller

1.1 Ferroelectric Transition in KH_2PO_4

The velocity and attenuation of 15 MHz shear waves propagating

perpendicular to the polar axis of KH_2PO_4 have been measured throughout the transition region. For that purpose, a low-temperature cell was built with provisions for poling the crystal with an electric field. Special care was taken to obtain a uniform electric field in the crystal by inserting a fused-quartz delay line between the transducer and the crystal. Measurements were carried out as a function of the applied electric field over the range 0-5 kv cm^{-1}.

The presence of domains in the ferroelectric phase caused intense scattering of the acoustic wave. For zero applied field, it was not possible to observe any signal immediately below the Curie temperature. For applied fields of 1 to 3 kv cm^{-1}, velocity measurements could be made throughout the transition region but the attenuation values were perturbed by sizeable scattering losses. Applied fields above 3 kv cm^{-1} were required to pole the crystal into a single domain, and excellent velocity and attenuation data were obtained in range 3 to 5 kv cm^{-1}.

An analysis of the data reveals some interesting new features concerning the polarization relaxation time, τ_p, particularly when it is compared with the value for the isomorphic crystal KD_2PO_4. Above T_c, the relaxation time τ_p in KH_2PO_4 is approximately 10 times shorter than the value in KD_2PO_4 whereas below the transition they are essentially equal. These results indicate that hydrogen tunneling is probably an important mechanism for the faster rate of relaxation in the paraelectric phase of KH_2PO_4. At present an attempt to interpret the data in terms of a microscopic theory of relaxation dynamics is in progress.

1.2 Liquid-Vapor Critical Point in Xenon

During the past year, considerable ultrasonic velocity and attenuation data have been obtained in the critical region. P. E. Mueller completed his doctoral thesis work with a series of isochoric measurements, and D. Eden is now engaged in carrying out a series of isothermal measurements. In addition, the electronics have been recently modified to permit more sensitive and more accurate measurements very close to the critical point.

In particular, the sensitivity of the ultrasonic equipment at 1 and 3 MHz has been greatly enhanced. Our new technique is a modification of existing coherent detection schemes applied to variable path measurements of ultrasonic pulses. The additional delay and the decrease in amplitude of an ultrasonic pulse caused by an increase in the length of the transmission path are precisely measured by phase comparison of the received ultrasonic signal at the carrier frequency. Phase-sensitive detection in a

balanced mixer provides a phase detector output which is linear, sensitive to small delay changes, and has a high signal-to-noise ratio. The accuracy of velocity measurements is better than 0.1% and the accuracy of attenuation values is typically ±0.7 dB cm^{-1}. Dr. R. C. Williamson was of great assistance in developing this technique.

Isothermal measurements of both velocity and attenuation have been made at 16.61° and 16.945°C at 1 MHz, and at 16.59°, 16.62°, and 16.67°C at 1 and 3 MHz. The velocity at 1 and 3 MHz and the attenuation at 1, 3, and 5 MHz have been determined along an isochore of mean reduced density $\rho/\rho_c \simeq .95$. In addition 1 MHz velocity and attenuation were measured for $\rho/\rho_c \simeq 1.03$. Velocities as low as 94.7 m sec^{-1} with attenuations of 0.404 nepers per wavelength (~375 dB cm^{-1}) have been observed at 1 MHz. There is a very noticeable velocity dispersion between 1 and 3 MHz in the immediate vicinity of the critical point. In addition, the ratio $\alpha_\lambda(3\text{ MHz})/\alpha_\lambda(1\text{ MHz})$ deviates from the classical value of 3 and approaches unity. Attenuations as high as 0.55 neper per wavelength (~1400 dB cm^{-1}) have been measured at 3 MHz.

2.0 Dynamical Calorimetry

Personnel: C. W. Garland; A. Bonilla

Phase-sensitive detection techniques have been applied to the measurement of heat capacities near a critical point. The sample is subject to a heat input at a fixed frequency ω and its temperature variation is detected with a thermocouple whose output is measured with a "lock-in" detector. This output signal, which is inversely proportional to the heat capacity of the sample, can be measured with considerable precision as a function of the mean sample temperature. The dynamic behavior of a system with oscillatory heat input is determined by two time constants. It is desirable that $\omega\tau_1 > 1$ and $\omega\tau_2 \ll 1$, where τ_1 is the relaxation time for heat flow between the sample and the surroundings and τ_2 is the characteristic time for the sample to reach internal thermal equilibrium.

Apparatus has been designed and test measurements are in progress on the application of this method to chromium near its antiferromagnetic transition.

3.0 Low-Temperature X-Ray Diffraction

Personnel: C. W. Garland; A. Bonilla

The lattice parameters of NH_4Br have been measured as a function of temperature from 5°K to 150°K, a range which includes the region of the transition between cubic and tetragonal ordered phases. The low-temperature CsCl-type phase exhibits normal thermal expansion up to ~108°K on warming, while the tetragonal diffraction pattern persists down to ~80°K on cooling. The present data are combined with previous measurements between 150°K and 300°K to yield an overall picture of the variations associated with changes in ordering. This work is now complete, and a manuscript describing our results should appear soon in Acta Crystallographica.

4.0 Pressure-Volume Measurements

Personnel: C. W. Garland; B. Weiner

A high-precision capacitance method of measuring the change in length of a single crystal as a function of pressure has been developed and applied to NH_4Cl near its "lambda" line. A large quantity of data have been obtained at five different constant temperatures between 250 and 270°K. These observations clearly confirm the existence of a first-order transition along the low-pressure end of the order-disorder transition line. At 1 bar and ~242°K, it is definitely known (from X-ray and from capacitance data) that there is a discontinuity in the volume: $\Delta V/V = 4.8 \times 10^{-3}$. At 1000 bar and ~252°K, this first-order discontinuity is much smaller ($\Delta V/V = 1.6 \times 10^{-3}$), and $\Delta V/V$ is probably zero and certainly less than 0.2×10^{-3} at 258°K at 1700 bar.

At temperatures greater than 258°K and corresponding transition pressures greater than 1700 bar, there is no longer a first-order character to the transition. Between 1700 and 2500 bar, the transition appears to be of the classical lambda type. In other words, the V(p) curves exhibit an infinite slope but no discontinuity. Above ~2500 bar the volume variation is still rapid but not infinitely so. Preliminary work in this region indicates the transition is second-order in the Ehrenfest sense.

Theses:

P. E. Mueller, "Ultrasonic Velocity and Attenuation in Xenon near its Liquid-Vapor Critical Point", Ph.D., Department of Chemistry, June 1969.

Publications:

C. W. Garland and R. A. Young, "Elastic Constants of Ammonium Bromide. II. High-Pressure Ultrasonic Investigation of the Phase Transitions",

J. Chem. Phys. 49, 5282 (1968).

C. W. Garland and D. B. Novotny, "Ultrasonic Velocity and Attenuation in KH_2PO_4", Phys. Rev. 177, 971 (1969).

C. W. Garland and N. E. Schumaker, "Infrared Investigation of Ordering and Structural Changes in Ammonium Halides", Molecular Dynamics and Structure of Solids, NBS Special Publ. No. 301, p. 241 (1969).

A. Bonilla, C. W. Garland, and N. E. Schumaker, "Low-Temperature X-Ray Investigation of NH_4Br", Acta Cryst. A25,___ (1969).

C. W. Garland and D. D. Snyder, "Ultrasonic Attenuation near the Lambda Transition in NH_4Cl at High Pressures", J. Phys. Chem. Solids, to be published.

XII. CRYSTAL AND SURFACE STRUCTURE INVESTIGATIONS in Metals, Zeolites, and Other Substances by X-Ray, Neutron, and Low Energy Electron Diffraction

Faculty:

D. P. Shoemaker, Professor, Chemistry

Research Staff:

Dr. Clara B. Shoemaker, Research Associate, Chemistry

Graduate Students:

P. C. Manor, Research Assistant, Chemistry

R. A. Ogilvie, Research Assistant, Chemistry

J. Bartley, Teaching Assistant, Chemistry

Support Staff:

Janet Pollock, Secretary, Chemistry

Personnel who have left:

Dr. Yu. V. Voroshilov, Visiting Scientist, Chemistry (now at University of Lvov, USSR)

M. A. Taylor, Research Assistant, Chemistry (now at Bradley University, Peoria, Ill.)

Degrees Granted:

M. A. Taylor, Ph.D., Chemistry, February 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 78883

Army Research Office (Durham), DA-31-124-ARO(D)-358, DSR 74966

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 (Army)

The crystal structure of the nu phase $Mn_{81.5}Si_{18.5}$ (Immm, a = 17.01,

b = 28.76, c = 4.65 A, 186 atoms per unit cell) has been fully refined (to R = 0.045). The atomic arrangement as in structures determined earlier in this program is characterized by exclusively tetrahedral interstices and atomic near-neighbor coordination numbers of 12, 14, 15 and 16. The structure is closely related to that of the P phase (Mo-Ni-Cr).

The crystal structure of a phase in the Mn-Co-Si system has been determined. The crystal specimen was taken from a sample of Q phase of approximate composition $Mn_{45}Co_{40}Si_{15}$ kindly furnished by Professor Paul A. Beck, but it appears likely that the structure determined is actually that of the Y phase of a nearby composition (somewhat richer in Si), a phase designated X by Russian workers, and that our Q phase sample contains crystals of Y. The structure, with space group Pnnm, a = 15.37, b = 12.26, c = 4.76 A, 74 atoms per unit cell, was determined by the Karle and Karle symbolic addition method. This structure also has only tetrahedral interstices and CN 12, 14, 15, and 16, and is very closely related to the Laves phases.

2.0 Fundamental Studies in the Field of Aluminas, Molecular Sieves, and Related Materials (Humble)

A body-centered cubic structure (a = 15.3A, Im3m) has been found for a synthetic zeolite, and a reasonable fit has been obtained between observed and calculated powder intensities. Refinement is in progress.

3.0 Low-Energy Electron Diffraction (NSF, ARPA)

Analysis of the intensity of the 00 reflection from Zn 0001 at near normal incidence as a function of temperature has indicated that atomic thermal motion increases in the immediate vicinity of the surface. Apparent Debye temperatures (corresponding to thermal motion normal to the 0001 plane) range from 127°K at 92 volts beam energy to 191°K at 400 volts, demonstrating an increase with effective depth of electron penetration; the bulk value is 235°K. Intensity vs. voltage curves for the 00 reflection at near normal incidence show nominally "forbidden" odd orders of 000ℓ, as predicted by the theory of Gerlach and Rhodin.

4.0 Other Crystal Structure Studies

In order to determine the conformation and absolute configuration of the (-) trans-cyclooctene molecule C_8H_{14}, the crystal structure of the

derivative used in previous resolution work of A. C. Cope and coworkers, the diastereomeric pi complex $C_8H_{14}\cdot PtCl_2NH_2CHCH_3C_6H_5$, is being determined. Preliminary results (R = 0.10) indicate strongly that the ring has staggered rather than eclipsed configurations around the 3, 4 and 7, 8 single bonds (related by C_2 molecular symmetry) and that the absolute configuration is that predicted for it by Cope on chemical evidence rather than the contrary theoretical prediction of Moskowitz and Mislow. Refinement is continuing.

The structure of a pyrochlore analogue, $BiCd_2Cl_6\cdot 5H_2O$, is being studied in order to elucidate the positions of the water molecules, which are to some degree zeolitic (capable of being reversibly removed from the crystal without breakdown of the crystal structure). Tentative H_2O oxygen positions have been established. At atmospheric humidity close to deliquescence the crystals show strong primary extinction, which can establish itself in seconds on exposure of a normally mosaic crystal to moist air, and disappear in seconds on reversion to the initial conditions.

Thesis:

M. A. Taylor, "A Low-Energy Electron Diffraction Study of Cleaved Zinc Surfaces", Department of Chemistry, February 1969.

Publications:

W. B. Pearson and C. B. Shoemaker, "A System of Coding and Generating of Layered, Tetrahedrally Close-Packed Structures", Acta Cryst. B25, 1178 (1969).

C. B. Shoemaker and D. P. Shoemaker, "Structural Properties of some Sigma-Phase Related Phases", Chapter in "Developments in the Structural Chemistry of Alloy Phases" (ed. by B. C. Giessen), New York: Plenum Press, 1969.

D. P. Shoemaker and G. Bassi, "On Refinement of the Crystal Orientation Matrix and Lattice Constants with Diffractometer Data", Acta Cryst. A25, in press (1969).

D. P. Shoemaker, "On Refinement of the Crystal Orientation Matrix and Lattice Constants with Diffractometer Data, II." Submitted to J. Applied Cryst. (1970).

XIII. MOLECULAR CRYSTALS

Faculty:

R. J. Silbey, Associate Professor, Chemistry

Research Associates:

J. S. Alper (Sept. 1, 1968 - Aug. 31, 1969)

B. Sharf (Sept. 1, 1969 -)

Graduate Students:

M. Grover, NSF Predoctoral Fellow, Chem.

P. Chalmer, NSF Trainee, Chem.

J. Schroeder, Research Assistant, Chem.

C. Sloane, Research Assistant, Chem.

S. Rackovsky, NSF Predoctoral Fellow, Chem.

J. Herzfeld, Research Assistant, Chem.

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75108 (from February 1, 1968)

National Science Foundation, GP-8387, DSR 70993 (from June 1, 1968)

Petroleum Research Fund of American Chemical Society, #3574-A5, DSR 71152 (from Sept. 1, 1968

Research Report:

During the past year, work has continued on the exciton phonon interaction in molecular crystals and its relationship to line shapes and energy transfer. In these crystals, the coupling of these modes may be strong, and we have derived a theory which takes this into account using the Green's function formalism. The qualitative details of line shapes are in agreement with experiment, and calculations are underway to test the theory further. We have also begun work on energy transport in these solids.

We have also done some work on electron-phonon interactions in molecules. This work, which was an off-shoot of our solids work, concentrated on a description of the Jahn-Teller effect in molecules, in particular the case of a doubly degenerate vibration interacting with a doubly degenerate

electronic state. We found two different unitary transformations which partially diagonalized the hamiltonian and give good agreement with exact calculations. We have also applied this technique in the case of nearly degenerate electronic levels ("pseudo" Jahn-Teller effect). Again the agreement is good. Our method is much simpler than the machine computations, and give comparable accuracy to other more complex methods.

The above work has now been written up and will appear in Journal of Chemical Physics shortly.

XIV. MOLECULAR SPECTROSCOPY

Faculty:

R. C. Lord, Professor, Chemistry

Research Staff:

I. Harada, Research Associate, Chemistry
D. W. Wertz, Research Associate, Chemistry
Anne-Marie Bellocq, Research Associate, Chemistry

Graduate Students:

C. C. Milionis, Research Assistant, Chemistry
W. J. Adams, Research Assistant, Chemistry
T. L. Berman, Research Fellow, Chemistry
L. A. Carreira, Research Assistant, Chemistry
D. C-M. Luk, Research Assistant, Chemistry
C. W. Wickstrom, Research Assistant, Chemistry
N-T. Yu, Norris Research Fellow, Chemistry
C. S. Blackwell, Teaching Assistant, Chemistry
R. Mendelsohn, Research Assistant, Chemistry
T. Ikeda, Research Assistant, Chemistry
Victoria R. Sauer, Research Assistant, Chemistry
T. C. Rounds, Teaching Assistant, Chemistry
C. J. Wurrey, Teaching Assistant, Chemistry

Support Staff:

Ruth C. Deininger, Secretary, Chemistry

Degrees Granted:

L. A. Carreira, Ph.D., Chemistry, June 1969
D. C-M. Luk, S.M., Chemistry, September 1969
C. C. Milionis, Ph.D., Chemistry, September 1969
N-T. Yu, Ph.D., Chemistry, September 1969

Sponsorship:

Spectroscopy Laboratory: National Science Foundation, GP-4923-X2, DSR 71804

Spectroscopy Laboratory: National Institutes of Health, 1 R01 GM15310-03
BBCB, DSR 71907

Research Report

1.0 Studies in Far Infrared Spectroscopy

1.1 Investigation of Molecules with Strongly Anharmonic Potential Functions

Far infrared spectra of a number of ring molecules having potential functions associated with inversion of the ring have been observed for the first time. In addition to some four- and five-membered rings whose potential functions are symmetrical, spectra of several with asymmetrical functions have now been analyzed. These include azetidine (4-ring), 2,5-dihydropyrrole (5-ring) and cyclopentene epoxide (6-ring). The asymmetry introduces complications into both the spectra and the mathematical treatment of the results, but it appears that reliable potential functions can be obtained from the spectra. A principal objective of these studies is the measurement and understanding of the sources of conformational energy differences in ring molecules. Since the barriers studied to date in the far infrared have values of less than 3 kcal, they fall in a range different from those measured by present nmr techniques, which are usually above 7-8 kcal.

In addition to inversion, the phenomenon of pseudo-rotation is currently under investigation in various five- and six-membered rings. The molecules cyclopentanone and thiacyclopentane have been investigated and their spectra analyzed in terms of hindered pseudo-rotation. Other molecules currently under study are 1,4-dioxo-2,5-cyclohexadiene, 3-thietanone and 1,1-difluorocyclobutane.

The supposedly linear molecule carbon suboxide has been found to have absorption in the far infrared which must arise from a strongly anharmonic potential function for molecular bending. This absorption shows considerable structure over the range 20-80 cm^{-1}, which resembles in its rotational contours those bands examined at high resolution in the mid infrared. A computer program has been written to enable calculation of these contours, and with the appropriate values of the molecular constants the program reproduces the observed contours fairly well. The molecular constants are also consistent with the gaseous entropy as determined thermodynamically. This work is being prepared for publication.

2.0 Infrared and Raman Studies of Compounds of Biophysical Interest

The laser-excited Raman spectra of a number of substances of biological importance have been obtained. The enzyme lysozyme has been studied in aqueous solution over a range of temperatures up to 60°C and of pH from 2 to 9. Spectra of the constituent amino acids in both monomeric and oligomeric form have also been recorded, with the objective of finding which Raman lines in lysozyme can be ascribed to conformation-independent frequencies of the constituent peptides and which are sensitive to the conformation of the protein. As an example of the former there may be cited the intense indole ring lines in the Raman spectrum of the amino acid tryptophane, which show up clearly and unaltered in frequency in the spectrum of lysozyme.

Investigation of the association of DNA bases with physiologically active compounds in chloroform solution has continued. A number of drugs related to the barbiturates and hydantoins have been examined, though no association constants larger than those already measured for the principal barbiturates with adenine were found. The association of hypoxanthine with other nucleic acid derivatives has also been measured.

A study of the far infrared and Raman spectra of single crystals of dimers formed between 9-methyl adenine and 1-methyl thymine has been carried out, together with a study of the crystals of each constituent separately. With the help of a normal-coordinate treatment of the sort first used for molecular crystals by Shimanouchi and his school, the low-frequency spectra of the complex have been analyzed with some degree of reliability. The results of such studies will eventually be important in analysis of the low-frequency vibration spectra of RNA and DNA.

Theses:

L. A. Carreira, "Far Infrared Spectra of Ring Compounds with Asymmetric Potential Functions for Inversion", Ph.D., Department of Chemistry, June 1969.

D. C-M. Luk, "Infrared Studies of Association of Some Nucleic Bases", S.M., Department of Chemistry, September 1969.

C. C. Milionis, "High-Resolution Study of the Far-Infrared Spectrum of Gaseous Carbon Suboxide", Ph.D., Department of Chemistry, September 1969.

N-T. Yu, "Infrared and Raman Spectra of Some Biopolymers and Related Molecules", Ph.D., Department of Chemistry, September 1969.

Publications:

Y. Kyogoku, R. C. Lord and A. Rich, "An Infrared Study of the Specific Hydrogen Bonding of Hypoxanthine with Other Nucleic Acid Derivatives", Biochim. Biophys. Acta 179, 10 (1969).

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L. A. Carreira and R. C. Lord, "Far Infrared Spectra of Ring Compounds. IV. Spectra of Compounds with an Unsymmetrical Potential Function for Ring Inversion", J. Chem. Phys. 51, 2735 (1969).

L. A. Carreira and R. C. Lord, "Far Infrared Spectra of Ring Compounds. V. Ring-Puckering Potential Functions of Some Oxygen-Containing Molecules", J. Chem. Phys. 51, 3225 (1969).

D. W. Wertz, "Far-Infrared Absorption Spectrum and Pseudorotation of the Thiacyclopentane Molecule", J. Chem. Phys. 51, 2133 (1969).

I. Harada and R. C. Lord, "Low-frequency Infrared and Raman Spectra of Some Adenine and Uracil Crystals", Spectrochimica Acta, in press.

XV. MICROWAVE SPECTROSCOPY

Faculty:

M. W. P. Strandberg, Professor, Physics
R. L. Kyhl, Professor, Electrical Engineering

Research Staff:

Julian G. Ingersoll, DSR Staff, R.L.E.
John D. Kierstead, DSR Staff, R.L.E.

Students:

James B. Barton, Research Assistant, Physics
Jerald Berman, Research Assistant, Physics
Leslie R. Fox, Research Assistant, Physics
John U. Free, Research Assistant, Physics
Robert M. Langdon, Jr., Research Assistant, Physics
Bell N. Yung, Research Assistant, Physics
Gerald Rappe, Doctor's Thesis Student, Chemical Engineering
Shirley A. Jackson, Graduate Student, Physics
James M. Smith, Graduate Student, Physics
Barrett A. Eisenstat, Undergraduate Thesis Student, Physics
Oliver U. Mobisson, Undergraduate Thesis Student, Mechanical Engineering
Robert L. Woerner, Undergraduate Thesis Student, Physics

Support Staff:

Alexander Bowens, Laboratory Assistant, R.L.E. (part-time)
William J. Schwabe, Senior Technician, R.L.E.
Irene A. Olasz, Secretary, R.L.E.

Personnel who have left:

Alexander Bowens
Barrett A. Eisenstat
Julian G. Ingersoll
Shirley A. Jackson
Oliver U. Mobisson
Gerald Rappe
Bell N. Yung

Sponsorship:
Research Laboratory of Electronics, supported in part by the Joint Services Electronics Program under Contract DA 28-043-AMC-02536(E), DSR 7-0050.

Research Report:

1.0 Metals

The variation of electromagnetic surface impedance of metal single crystals at low temperatures with applied magnetic field is being studied. Theoretical and experimental analyses are being carried out to investigate the transport properties of these crystals under these conditions. Experimental work has demonstrated the usefulness of this technique in measuring the wave vector dependence of the temperature-dependent electron mean-free paths in these materials and for studying the angular dependence of the specular reflection coefficient.

2.0 Microwave Ultrasonic Studies

Acoustic propagation in metals at microwave frequencies is being studied. Preliminary experiments indicate that the effect of boundary-layer scattering, lattice imperfection scattering, and electron scattering can be separated from one another by observing the frequency dependence of the acoustic transmission coefficient of thin films.

3.0 Noise in Superconducting Bolometers

Present studies are directed at understanding sources of noise beyond that accounted for by Johnson noise and temperature fluctuation noise in superconducting bolometers. At present, we are focusing on a study of the fluctuation in the entropy transport by means of magnetic field vortices. This entropy transport mechanism may possibly yield an explanation for the anomalous temperature fluctuation noise observed in these bolometers at zero magnetic field, which is suppressed by the application of a magnetic field of the order of a few Gauss.

Degrees Granted:

Barrett A. Eisenstat, B.S., Physics, June 1969.
Oliver U. Mobisson, B.S., Mechanical Engineering, June 1969.

Gerald Rappe, D.Sc., Chemical Engineering, September 1969.
Bell N. Yung, Ph.D., Physics, September 1969.

Theses:

B. A. Eisenstat, "A Study of Electromagnetic Oscillations in Spherical Cavities," B.S. Thesis, Department of Physics, June, 1969.

O. U. Mobisson, "Fabrication of Thin Film Superconducting Bolometers," B.S. Thesis, Department of Mechanical Engineering, June, 1969.

G. C. Rappe, "Hydrogen Atom Addition to Solid Isobutylene at 77°K," D.Sc. Thesis, Department of Chemical Engineering, September, 1969.

B. N. Yung, "The Propagation of Electromagnetic Waves in Metal Single Crystals," Ph.D. Thesis, Department of Physics, September, 1969.

The following are abstracts of theses published in the R.L.E. Quarterly Progress Report, M.I.T.:

B. A. Eisenstat, "A Study of Electromagnetic Oscillations in Spherical Cavities," QPR 94, pp. 13, Research Laboratory of Electronics, M.I.T., July 15, 1969.

O. U. Mobisson, "Fabrication of Thin-Film Superconducting Bolometers," QPR 94, pp. 13-14, Research Laboratory of Electronics, M.I.T., July 15, 1969.

Publications:

C. B. Friedberg and M. W. P. Strandberg, "Microwave Magnetoresistance Measurements," J. of Applied Physics 40, 6 (1969).

M. K. Maul and M. W. P. Strandberg, "Equivalent Circuit of a Superconducting Bolometer," J. of Applied Physics 40, 7 (1969).

S. R. Reznek and M. W. P. Strandberg, "Surface Impedance and Boundary Scattering in Metals for the Conditions of the Anomalous Skin Depth," Phys. kondens. Materie 9, 158 (1969).

M. K. Maul, M. W. P. Strandberg, and R. L. Kyhl, "Excess Noise in Superconducting Bolometers," Phys. Rev. 182, 522 (1969).

Papers submitted for consideration for publication:

B. N. Yung and M. W. P. Strandberg, "Role of Specular Reflection of Electrons in the Radio Frequency Surface Magneto Impedance of Metals," Physical Review Letters.

Meeting papers presented during 1969:

"Microwave Magnetoresistance Measurements," presented at the National Jubilee Conference on Electron Paramagnetic Resonance, Kazan, U.S.S.R., June 24 - 29, 1969, by M. W. P. Strandberg.

CHEMICAL AND SOLID STATE PHYSICS

XVI. OPTICAL AND INFRARED LASERS

Faculty:

A. Javan, Professor, Physics
A. Szöke, Associate Professor, Physics
M. Feld, Assistant Professor, Physics
N. Kurnit, Assistant Professor, Physics
R. Brewer, Visiting Professor, Physics

Research Staff:

L. Hocker, DSR Staff, Physics
S. Iwasa, DSR Staff, Physics
J. Lifsitz, DSR Staff, Visiting, Physics

Graduate Students:

T. Ducas, Research Assistant, Physics
B. Feldman, Research Assistant, Physics
R. Francke, Research Assistant, Physics
L. Geoffrion, Research Assistant, Physics
H. Grieneisen, Brazilian Fellowship, Physics
M. Guerra, Research Assistant, Physics
F. Harbus, NSF Fellowship, Physics
M. Kelly, Research Assistant, Physics
J. Levine, Research Assistant, Physics
F. Missell, Research Assistant, Electrical Engineering
J. Monchalin, Research Assistant, Physics
J. Murray, Research Assistant, Physics
R. Osgood, Research Assistant, Physics
A. Sanchez, Research Assistant, Physics
N. Skribanowitz, Research Assistant, Physics
D. Sokoloff, NSF Fellowship, Physics

Undergraduate Students:

D. Carlin, Research Assistant, Physics
J. Goldhar, Research Assistant, Physics

Support Staff:

L. Ryan, Jr., Engineering Assistant, Physics
B. Billings, Administrative Assistant, Physics
G. Mazzarella, Technical Assistant, Physics
M. Menton, Secretary, Physics

Personnel who have left:

R. Brewer, Visiting Professor, Physics (Now at IBM Research Laboratory, San Jose, California)
G. Koppelmann, Visiting Associate Professor, Physics (Now at Technischen Universitat Berlin, Germany)
V. Daneu, DSR Staff, Physics (Now at Instituto di Eltrotechnica, Palermo, Italy)
M. Kovacs, Research Assistant, Physics (Now at United Aircraft Research Laboratories, East Hartford, Connecticut)
C. Rhodes, Research Assistant, Physics (Now at T.R.G., Long Island, New York)
J. Small, Research Assistant, Physics (Now with German Army)
R. Solomon, Administrative Assistant, Physics (Now at Fairchild, San Francisco, California)

Degrees Granted:

M. Kovacs, Ph.D., Physics, September 1969
C. Rhodes, Ph.D., Physics, September 1969
P. Schroeder, Ph.D., Physics, September 1969

Sponsorship:

National Aeronautics and Space Administration, NGL-22-009-012, DSR 76148
Air Force Cambridge Research Laboratories, F19(628)-68-C-0204, DSR 72075
Office of Naval Research, N00014-67-A-0204-0014, DSR 70620
U. S. Army Research Office, DAHC04-68-C-0022, DSR 70950

Research Report

The Optical and Infrared Laser Research Group engages in a comprehensive research program employing various types of gas lasers. The group's activities encompass a broad range of the electromagnetic spectrum extending from the submillimeter, through the infrared and visible, and down into the ultraviolet. A unified approach is adopted in the exploration

of a varied set of problems. In this approach, fundamental research objectives and related problems in applied research have evolved together, often requiring the development and perfection of new devices and techniques. The activities of the group may be subdivided into several broad categories, each consisting of several experiments:

1.0 Measurement of the Frequency of Light
2.0 Nonlinearities of Atomic and Molecular Resonances
3.0 Transmission and Generation of Short Duration Pulses
4.0 Studies of Excitation and Relaxation Mechanisms in Atoms and Molecules
5.0 Studies in High Magnetic Fields

1.0 MEASUREMENT OF THE FREQUENCY OF LIGHT

1.1 Developments of Infrared Point-Contact Rectifiers and Frequency Mixer Diodes; Applications in Laser Harmonic Frequency Mixing

For the first time at infrared frequencies, a special fast response point-contact rectifier and mixer diode (response time $\tau \lesssim 3 \times 10^{-14}$ sec.) is developed and used to mix the high order harmonics of an infrared laser with the fundamental frequency of another infrared laser and a microwave intermediate frequency. The diode is used as a lumped circuit element at the infrared frequencies much the same as the rectifiers and frequency mixing diodes are used at the microwave frequencies. The experiment provides the crucial technique necessary to establish a frequency multiplier chain for comparing the frequency of short wavelength infrared radiation with that of a standard microwave clock--an area of considerable importance in establishing an ultimate connection between the length and time standards. Furthermore, harmonic frequency mixing of this type provides a means of comparing two widely differing infrared frequencies with an accuracy surpassing considerably that of the previous standard means of wavelength comparison. The experiment also gives a direct proof that the special frequency mixing element acts as a diode with nonlinear characteristics which allows alternating currents to flow through its junction at frequencies as high as 3×10^{13} cycles/sec--a development which makes possible the extension of most microwave rectification and frequency mixing techniques into the infrared region. In the experiment, the output of a 28.0μ water vapor laser is mixed in the diode with that of a 9.3μ CO_2 laser and a K-band microwave klystron radiation. A strong beatnote is observed when the klystron frequency is tuned to the difference between the frequency

of the 9.3μ laser and the third harmonic of the 28.0μ laser.

The diode element consists of a thin tungsten wire antenna--about two microns diameter and several millimeters long--mounted at the end of a coaxial cable, its tip pointed by means of a standard etching technique, and contacted mechanically with a nickel (or cold-rolled steel) post mounted on a differential screw to allow fine adjustment of the point contact. The laser radiations and the microwave klystron output are coupled to the diode's thin wire antenna; the mixing beatnote and the infrared rectification signal voltages are observed across the diode. It is believed that the tungston-metal point contact occurs through a thin oxide layer and the tunneling of the electrons across the layer is responsible for the nonlinear voltage-current characteristics leading to the infrared rectifications and frequency mixing. Experiments are underway to establish the details of the processes.

The above diode is applied in a variety of other frequency mixing experiments at lower frequencies. For instance, an 84μ D_2O laser is mixed in the diode with the output of a 337μ HCN laser and a microwave radiation at C-band (5.9GHz); here, the fourth harmonic of the 337μ laser frequency differs from the 84μ laser frequency by 5.9GHz. The 84μ laser frequency is then determined by mixing the 337μ laser with a high order harmonic of a microwave klystron frequency at V-band.

The success in frequency mixing of the 9.3μ and 28.0μ lasers ensures the application of the diodes in similar laser harmonic frequency mixing at least up to the 9μ limit. Accordingly, frequency multiplier chains may now be established for the measurements of the absolute frequencies up to this limit. It is likely that the point-contact diode of the type described here may have response limits considerably above the 9μ region; additional experiments are required to establish the upper limits.

It should be noted that frequency multiplication from 10μ towards the visible region has been possible for some time through the use of bulk nonlinearities--a well-known technique which has already been used, for example, in tripling the 10μ CO_2 laser frequency. However, frequency mixing and multiplication below the 10μ region has required the development of an entirely different approach based on the development and application of the infrared and far infrared diodes. Accordingly, the closing of the gap up to the 9μ region makes possible the application of already existing means to the frequency comparison of a near infrared (or possibly a visible) laser with that of a microwave clock.

In addition to a variety of applications in precision spectroscopic studies, absolute frequency measurements in the infrared and the visible range have important applications in the area of establishing a firm connec-

tion between the length and time standards and in precise determination of the speed of light. It must also be noted that recent experiments based on the inverted Lamb-dip have made available a family of narrow resonances in the infrared and the visible region which are particularly suitable for reproducible frequency resettings of appropriate gas lasers with a high degree of accuracy; comparison of these laser frequencies with a microwave clock makes these resonances interesting candidates for use as primary time standards.

1.2 Precise Determination of the Speed of Light

Considerable progress has been made in our speed of light experiment. The measurement is being made by simultaneously determining the frequency and wave length of an 84μ D_2O laser. The frequency of the laser is measured by mixing it with the 337μ HCN laser frequency and a suitable microwave frequency. The wavelength is determined by comparison with the wavelength of a stabilized 6328Å laser and a Michelson interferometer (constructed at Perkin-Elmer). A digital computer is utilized to analyze the output of the interferometer to provide a precise determination of the ratio of the wavelengths of the infrared and visible lasers.

At the present time the frequency measuring apparatus at 84μ is in working condition. Insofar as the wave length measurements are conserned, considerable progress has been made in the last month in eliminating several serious effects. The problem of feedback of 84μ radiation from the Michelson interferometer back into the laser has been overcome by means of attenuators. The low frequency detector noise has been eliminated by mounting the detector on a piece of mylar to isolate it from the cold finger. This eliminates temperature fluctuations caused by the bubbling. The computer program to analyze the fringes of the 84μ and 6328Å lasers is now running very well. A preliminary determination of the speed of light should be made in the near future.

With the recent extension of laser harmonic frequency mixing up to the 9μ limit, the above measurement may be shifted from the 84μ to the 10.6μ. This possibility is now under consideration.

2.0 NONLINEARITIES OF ATOMIC AND MOLECULAR RESONANCES

2.1 Laser-Induced Line Narrowing Effects in Spontaneous Emission in Neon

This experiment is part of a continuing program aimed at measuring radiative parameters, collision cross-sections and atomic and molecular

constants by means of laser-induced line-narrowing techniques. The output of a high power single-mode 1.15μ He-Ne laser is focused into a low pressure Ne sample cell. The lineshape of spontaneous emission from the sample cell at 6096Å is observed along the axis of the incident beam by means of a high-resolution Fabry-Perot interferometer. Since the lower level of the 1.15μ transition is the upper level of the 6096Å transition, the laser field produces narrow 6096Å change signals superposed on the usual Doppler broadened background. If the applied laser field is in the form of a travelling wave a single change signal is observed. If it is in the form of a standing wave, two change signals of different widths appear symmetrically located on opposite sides of 6096Å center frequency.

In an earlier version of this experiment, the 6096Å emission signal from the He-Ne mixture within the laser cavity itself was observed. Consequently, only a very restricted range of pressure conditions could be studied. In the present arrangement it is possible to vary the pressure of pure Ne (or mixtures) over a wide range, including very low pressures ($\sim 10^{-3}$torr). It is thus possible to accurately measure radiative widths, collision broadening and pressure shifts.

The change signals from the external sample cell were first detected about four months ago. Since then their quality has been significantly improved. Improvements were made in optics (longer focal length lens to image sample cell), increased Fabry-Perot efficiency (by going to lower reflectivity mirrors), increased size of central maximum of Fabry-Perot (by slightly increasing instrumental linewidth) and increased signal intensity (by removing one of the two 6096Å interference filters). At present a signal noise ratio of 10:1 is obtained at a sample cell pressure of $\sim$20 microns with a 0.1 sec. time constant. The corresponding line widths are below 100 Mhz, about 25 times smaller than the Doppler widths. Preliminary measurements of pressure broadening and width differences between broad and narrow signals have been made. At the present time we are beginning to set up for final measurements of pressure broadening and pressure shifts.

2.2 High Resolution Stark Spectroscopy in Ammonia Using Nonlinear Techniques

Recently we have observed extremely narrow Lamb-dip resonances in stark-tuned transitions of the NH_2D molecule. In this experiment the P(20) CO_2 laser line is used to produce a quasi-standing wave field in an external cavity containing NH_2D at a low pressure. By sweeping the stark field up to about 11 e.s.u., it is possible to tune the sample through four resonances corresponding to the stark components of the $5_{14}(s) - 4_{04}(a)$

transition of the ν_2 vibration. As the center frequency of a stark transition is tuned to within a natural width of the frequency of the applied standing wave field a narrow Lamb-dip change signal occurs. The width of the change signal, 1.5 MHz, is about 60 times smaller than the Doppler width.

At the present time several improvements and modifications are being made. Using a more efficient chemical reaction we are trying to increase the NH_2D concentration, which was previously only about 1:200. Thus, it should be possible to considerably enhance the change signals. We are also in the process of studying Lamb-dip resonances in several other transitions in NH_2D which coincide with the P(14), P(16) transitions of the CO_2 laser. Transitions in NH_3 are also being explored.

2.3 Theory of a High-Intensity Gas Laser

A semiclassical theory of a single-mode gas laser, valid for essentially arbitrary values of field intensity, has been formulated. The theory is formulated in terms of an ensemble-averaged form of the density matrix equations of motion involving a single set of coordinates. The polarization and the population inversion density are expanded in spatial Fourier components. One obtains a set of coupled difference equations in the Fourier coefficients, y_n, which may be solved subject to appropriate boundary conditions on y_n for large n. The solutions may be expressed in terms of continued fractions in the general case, and in closed form in important special cases. Quantities of interest are evaluated by computer. The steady-state laser intensity and frequency are obtained from the coupled E. M. field equations as functions of the cavity parameters and the linear gain of the amplifying medium. At moderate values of field intensity the velocity distribution of the space-averaged population inversion density exhibits a fine structure for low velocity atoms superimposed on the usual broader depletion. This structure is a manifestation of the coherent ringing of the amplifying medium. The results are compared with those obtained in the rate equation approximation; and with the recent work of Stenholm and Lamb. Discrepancies with the latter paper are explained.

Several interesting implications of these results are currently being explored.

3.0 TRANSMISSION AND GENERATION OF SHORT DURATION PULSES

3.1 Experiments with Short Light Pulses at 10.6μ

Strong and short coherent pulses of electromagnetic radiation propagate through extended absorbing media with anomalously low absorption

they are delayed and reshaped. Experimental results, together with a detailed theoretical explanation, for 10.6μ wavelength pulses through gaseous SF_6 have been obtained. The degeneracy of overlapping levels of SF_6 in that spectral region is important, and enables us to use a simple model to describe observed phenomena. We assume a continuous distribution of dipole moments. Results are particularly interesting in two regimes of excitation. One corresponds to very strong excitation and 20 absorption lengths in the medium: pulses sharpen at their leading edge, while their front part gets absorved. The other pertains to much lower excitation and only two absorption lengths: re-radiation can be distinguished and long delays result which qualitatively resemble the behavior of a two level system in self-induced transparency. Fairly conclusive agreement is obtained between a previous theoretical treatment of a homogeneously broadened multi-level medium, and experiment. The agreement is substantiated by computer calculations.

3.2 Bi-Stable Optical Element

A bi-stable optical element which is capable of producing very short pulses has been developed. The device, an optical resonator containing a saturable absorber, consists of two BaF_2 mirrors coated with a single $\lambda/4$ layer of Te in an enclosure which can be filled with various pressures of SF_6 gas, a strong saturable absorber of the P(16) transition of the 10.6μ CO_2 laser. In the simplest configuration the device, placed in the output beam of a Q-switched CO_2 laser operating on the P(16) line, produces a sharpening of the Q-switched envelope. This sharpening occurs because the resonator increases the field strength of the applied field within the enclosure, thus enhancing the bleaching characteristics of the absorber. Furthermore, under appropriate conditions of absorption coefficient and mirror reflectivity, a bi-stable operating regime can set in in which the device switches over discontinuously from a state of low-intensity and high-absorption to one of high-intensity and low-absorption, or vice versa. The switching time depends on the ringing time of the resonator and the parameters of the absorber, and can be as short as 10^{-9} -10^{-10} sec. In other configurations the device can produce variable length pulses, long pulses trains, logical operations on two signals, and memory functions.

4.0 STUDIES OF EXCITATION AND RELAXATION MECHANISMS IN ATOMS AND MOLECULES

4.1 Motional Narrowing Spontaneous Raman Scattering in Hydrogen

The effect of motional narrowing of the linewidth in the spontaneous vibrational Raman scattering in H_2 and D_2 molecules is observed and studied exhaustively. A frequency stabilized argon ion gas laser is used as the Raman light source and the Raman scattered linewidth is analyzed with a scanning Fabry-Perot and a photon correcting detection system. This experiment has also included detailed observations of the pressure shift and pressure broadening in several Raman scattered lines. The experiment is now near completion.

4.2 Far-Infrared Continuous-Wave Laser Oscillation in Pure Helium

A continuous wave infrared helium laser has been constructed which oscillates at 95.8μ and 216.3μ, corresponding to the $3^1P \rightarrow 3D$ and $4^1P \rightarrow 4^1D$ transitions, respectively. The active medium is a low pressure D.C. excited gas discharge of pure helium.

An important aspect of this laser is the fact that many of its features are essentially predictable from existing theoretical calculations in helium starting from the first principles of quantum mechanics. Furthermore, the He plasma has been extensively studied in the literature and considerable information is available on parameters such as electron energy distribution and electron mobility. Accordingly, a study of the excitation mechanisms has enabled accurate calculation of laser gain and output power starting from first principles. The results are remarkably in close agreement with the experimental findings over wide ranges of currents and the gas pressures.

Precise absolute frequencies determinations of the He laser are also in progress. These measurements will provide important tests of radiative corrections and relativistic effects in He.

4.3 Excitation in Atomic Hydrogen by Means of Dissociative Excitation Transfer

A study is being made of dissociative excitation transfer from Ne $1s_5$ metastables to hydrogen molecules in a liquid N_2-cooled low pressure neon-hydrogen discharge. The process favors production of excited hydrogen atoms of high average Kinetic energy in the n= 3 level. Theoretical considerations suggest that under optimum conditions population inversion should occur between the n=3 and n=2 levels (H_α transition) at the wings of the velocity distribution, where no re-absorption from the ground state to the n=2 level can occur. Cooling the discharge in a liquid N_2 bath enhances the expected inversion by narrowing the velocity distribution of the lower levels. Measurements are being made of spontaneous emission intensity and decay times in the afterglow of a pulsed discharge.

4.4 Studies of Molecular Vibrational Relaxation

Studies of energy transfer and vibrational relaxation in CO_2 has continued. These have included measurements of the diffusion of vibrational excitation of the 001 state through CO_2 (and through a variety of buffer gases). Also, the effect of the imprisonment of radiation and its pressure dependence of the (001) $\rightarrow$ (000) is studied in detail and compared with the theory. The measurements have also included detailed observations of the decay rate of the (100) level and its coupling to the nearly (020) levels.

5.0 STUDIES IN HIGH MAGNETIC FIELDS

5.1 Application of a Laser Magnetoreflection Spectrometer to a High Resolution Study of Graphite, Antimony and Bismuth

An infrared laser, which employs Ne, He-Ne, He-Xe, and He-Kr-Ne gas mixtures and which operates continuously at some forty-five wavelengths in the range $3.1069\,\mu \leq \lambda \leq 21.746\mu$, has been applied to high resolution magnetospectroscopy of semi-metal graphite, antimony (Sb), and bismuth (Bi). The experiment consists of measuring the reflectivity R at a fixed laser photon energy as a function of the slowly varying d.c. magnetic field. Furthermore, the first and second derivatives (dR/dH and d^2R/dH^2) are obtained by means of modulating the magnetic field. The laser amplitude is stabilized by the combination of a servo-iris control and a feedback scheme on the discharge current. The laser spectrometer is capable of overall resolution and sensitivity which surpass those of a conventional spectrometer by up to two orders of magnitude.

In the study of graphite, a new insight has been gained in the understanding of the complex K-point interband transition spectra in the low quantum limit. Firstly, the assignment of the carriers at the K-point of the Brillouin zone has been reversed from the holes to electrons. Secondly, in making the identifications of various transitions in terms of the Slonczewski-Weiss band model, certain forbidden transitions were found to have comparable strength to allowed transitions. A consequence of this is the assignment of the SW parameter $\gamma_3 = 0.29 \pm 0.02$eV, which indicates an unusually large trigonal warping of the graphite Fermi surface. Therefore, no form of perturbation theory is likely to handle the magnetic energy level structure in the vicinity of the K-point. In addition, the oscillatory reflectivity spectra associated with the zone corner H-point interband Landau level transitions have been measured. The study of the highly asymmetric lineshape is of much interest in that it provides a means of accurately determining the parameters γ_0 and Δ. Also, comparison thus far shows very little

difference between the magnetoreflection data of pyrolytic and single crystals of graphite.

In the case of Sb, the optical Shubnikov-de Haas effect is investigated using laser radiation. The effect derives from the oscillations in the optical conductivity which are periodic in (1/H), as is characteristic of the de Haas-van Alphen type phenomena.

The effect highes on and gains by a high degree of magnetic field homogeneity, low temperature, and monochromaticity and a preferential direction of polarization of the probing laser radiation.

In the previous investigations, the effect was seen only in the 10% vicinity of the plasma frequency ($\hbar\omega_p = 0.1$eV), where a lineshape reversal occurred as the laser frequency ω crossed ω_p. Recent measurements at $\sim 1.9^{o}$K has revealed a strikingly large dHS oscillation in the photon energy range $0.0670 \leq \hbar\omega \leq 0.3535$eV. The classical intraband picture of the dHS effect does not sufficiently explain the data, and a current theory invokes an additional contribution from a set of interband transitions with proper coupling and density of states in order to describe the phenomena over a so much broader energy range. The high resolution study of the interband transition spectra as well as the Azbel-Kanar cyclotron resonance spectra in bismuth is continuing.

Theses:

M. A. Kovacs, "Study of Relaxation Processes of the ν_3 - Band in CO_2," Ph. D. Thesis, Department of Physics, September 1969.

C. K. Rhodes, "Some Results on Coherent Optical Processes in Gases," Ph. D. Thesis, Department of Physics, September 1969.

P. R. Schroeder, "Magnetoreflection of Graphite Using an Infrared Laser Source," Ph. D. Thesis, Department of Physics, September 1969

Publications:

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ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES OF MATERIALS AND DEVICE APPLICATIONS

I. SOLID STATE STUDIES GROUP

Faculty:

G. W. Pratt, Jr, Professor, Electrical Engineering
Mildred S. Dresselhaus, Professor, Electrical Engineering
D. Adler, Associate Professor, Electrical Engineering
D. D. Buss, Assistant Professor, Electrical Engineering

Research Staff:

L. G. Ferreira, Research Affiliate, Electrical Engineering
N. J. Parada, Research Affiliate, Electrical Engineering

Graduate Students:

R. W. Brodersen, Graduate Student, Electrical Engineering
D. Cammack, Graduate Student, Electrical Engineering
E. Das, Graduate Student, Electrical Engineering
C. Gordon, Graduate Student, Physics
L. Johnson, Graduate Student, Electrical Engineering
T. Kaplan, Graduate Student, Electrical Engineering
B. Ketchledge, Undergraduate Student, Electrical Engineering
E. K. Li, Graduate Student, Electrical Engineering
P. G. McMullin, Graduate Student, Electrical Engineering
F. P. Missell, Research Assistant, Physics
D. A. Platts, Research Assistant, Electrical Engineering
C. L. Rieck, Research Assistant, Physics
D. Schroeder, Graduate Student, Electrical Engineering
A. Tachagumpuch, Graduate Student, Physics
J. C. Tsang, Teaching Assistant, Electrical Engineering
C. Whitney, Graduate Student, Electrical Engineering
H. P. H. Yuan, Research Assistant, Electrical Engineering

Support Staff:

Thalia Perrin, Secretary, Electrical Engineering

Personnel who have left:

D. D. Buss, Assistant Professor, Electrical Engineering (Now at Texas Instruments)
N. J. Parada, Research Assistant, (Now at University of Sao Paulo)

P. R. Schroeder, (Now at Bell Telephone Labs, Allentown, PA)

Degrees Granted:

L. Johnson, S.M., Electrical Engineering, June 1969

N. J. Parada, Ph.D., Electrical Engineering, Feb. 1969

P. R. Schroeder, Ph.D., Physics, Sept. 1969

Sponsorship:

Office of Naval Research, Nonr-1841(72); NR018-106, DSR 78721

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Advanced Research Projects Agency, SD-90, DSR 75114, DSR 75117, DSR 71624

U. S. Air Force, Lincoln Laboratories Account 11195

Research Report

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

The lasing output of optically pumped PbSe under an applied strain that splits the multi-valley degeneracy of the conduction and valence bands is being studied. Both longitudinal and transverse modes have been observed. At sufficiently large applied strain stimulated phonon emission should take place.

Ultrasonic frequency modulation of GaAS diode lasers has been achieved up to 470 Mc using quartz transduces and at 1 GH_z using CdS. Accurate measurements have been made at 150 Mc of the side bands and a modulation index of 6 has been achieved at 150 Mc giving a total frequency deviation of 900 Mc. Ultrasonic modulation is being studied both with pulsed and cw lasers. Detailed measurements have been made on the frequency changes of the laser during a pulse.

Frequency modulation of a CO_2 laser is being studied using Raman scattering near a resonance while modulating the frequency shift by perturbing the phonon spectrum of the scatter. This may lead to a modulation band width for CO_2 in the 10 GH_z range.

The dielectric constant $\varepsilon(k)$ and the density of states for PbTe have been calculated. They are in excellent agreement with the optical properties and photoemission measurements. The $\varepsilon(k)$ evaluation was done using the $k \cdot p$ interpolation method previously developed for vacancy states.

The velocity of sound is being measured in PbSnTe as a function of the size of the energy gap. The gap can be made to go through zero and open up again as the temperature is lowered. As this happens there is a substantial

redistribution of charge among the Bloch states. This is in turn reflected in a change in the elatic properties since the interatomic potenial is dependent on the charge distribution in the solid.

2.0 Correlation in Narrow Bands-Magnetoelectrics (ONR)

The McIrvine-Overhauser superlattice representation has been carefully investigated. It has been shown to lead to single determinantal states of lower energy than a single determinant of Bloch or Wannier functions do not satisy the usual Hartree-Fock type equations. This implies that for a narrow band system there exists a new type of Hartree-Fock function that will lead to lower energies than the Bloch or Wannier types. We are trying to determine these new functions.

The conductivity of amorphous materials is being studied using a cluster technique developed in this group. The frequency dependence of the conductivity predicted by the model agrees with experiment.

A study of the magnetoelectric effect is being carried out using a field theoretical approach. It has been established under what conditions such a coupling of electric and magnetic behavior can be achieved.

3.0 Optical and Magneto-Optical Study of Solids

The high resolution magnetoreflection technique using a helium-neon laser has provided a valuable tool for the study of the magnetic energy level structure of several semimetals. In the case of graphite, the magnetoreflection spectra using circularly polarized laser radiation between 0.069 and 0.224 eV was analyzed with particular emphasis on the special Landau level transitions that occur in the low quantum limit. To understand the complicated spectrum observed in the low quantum limit, a detailed magnetoreflection lineshape calculation was carried out based on the Slonczewski-Weiss band model. Through this calculation, an identification of the various intraband and interband Landau level transitions could be made. It was furthermore found that the intensity of certain "forbidden" transitions was large compared to that for the "allowed" transitions; in fact, the magnitude of the forbidden transitions was so large that no form of perturbation theory could be used to handle to the handle the magnetic energy level structure. By developing a "big matrix technique" it was possible to calculate reliably the relative intensity of forbidden and allowed transitions and the results of the calculation provided an accurate determination of the graphite band parameter γ_3. This parameter governs the coupling between

certain states in the Sloczewski-Weiss band model and completely controls the warping of the graphite Fermi surface. A study of several Fermi surface properties is now underway to connect this new Fermi surface information with experimental measurements. The "big matrix technique" developed for this graphite problem can be equally well applied to various intensity calculations involving other magnetic energy level structures.

This high resolution technique together with a low temperature capability down to 1°K have been applied to studying the optical de Haas-Shubnikov effect. Whereas this effect appeared in previous work as a ∿1% structure superimposed on a large magnetoplasma background, the present study in antimony has yielded oscillatons with two orders of magnitude greater intensity. This great enhancement of the de Haas-Shubnikov effect has made possible a lineshape study and the asymmetric lineshape observed in the magnetic field dependence of the reflectivity is well explained by a simple model for the magnetic energy levels associated with the electron pockets in antimony. Futher work is in progress to study quantitatively the dependence of the optical de Haas-Shubnikov effect on temperature, photon energy, crystal orientation and sample geometry.

The infrared reflectivity of arsenic has been calculated and correlated with Fermi surface, magnetoreflection and optical reflectivity measurements. These infrared properties are strongly affected by interband transitions across a small spin-orbit induced bandgap which was discovered in our magntoreflection studies. The unusually large intensity of this interband transition for light incident along the trigonal direction is due to the simultaneous occurrence of a large interband momentum matrix element and a high density of states. The results of this infrared reflectivity calculation are in very good agreement with the experimental infrared reflectivity data. In this work the Lax two-band model was used extensively to obtain band parameters needed in the reflectivity calculation. The magnetoreflection experiments demonstrated the success of the Lax model in describing the energy bands in the light mass directions; the present work shows that the two band model works surprisingly well even in the heavy mass direction.

The optical properties of aluminum have been calculated up to 5 eV to determine whether energy bands based on a one electron approximation could provide a quantitative fit to optical data. The energy band model was required to fit the Fermi surface as measured by the de Haas-van Alphen effect and to fit the location of the major peak in the imaginary part of the dielectric constant at ∿1.5 eV. Fortunately, the pseudopotential energy band model of Ashcroft provides an excellent fit to the Fermi surface data and also yields a peak in E_2 at the proper photon energy. This model was therefore

used to provide both the energy levels and the k dependent momentum matrix elements needed in the dielectric constant calculation. The good fit to the experimental data demonstrates the success of a one electron energy band approach to the calculation of the optical properties of metals. This work has also shown that the Fourier expansion method can be successfully applied to the representation of nearly free electron energy bands in metals.

4.0 Electrical Conduction in Amorphous Semiconductors (ARPA, ONR)

4.1 Band Structure and Electrical Properties of Amorphous Semiconductors

Amorphous semiconductors, even when highly pure, are characterized by large concentrations of electronic states which are localized by the effects of the positional disorder. Once localized states are present, the Franck-Condon principle requires different electrical and optical densities-of-states. Furthermore, in localized states there is always a difference between ionization potential and electron affinity, a correlation effect, neglected in one-electron energy-band theory. Thus, band models for amorphous semiconductors can be quite misleading. We have modified the one-electron band modles of Mott and Cohen in order to explicitly take into account electronic correlations and the electron-lattice interactions. In amorphous Ge and Si, such a model explains the apparent sharpness of the optical spectrum formerly considered to be in conflict with the ideas of band-tailing in disordered materials. The main reasons for the sharp band edge is the effective upward displacement of the localized tail of the conduction band due to intraatomic electronic correlations taken together with the electron-phonon stabilizations of the occupied states in the valence band tail. In the covalent amorphous semiconductors, the model of Cohen, Fritzsche and Ovshinsky predicts an overlap of localized states from the valence and conduction band tails somehwere in the center of the gap. When correlations, polaron formation and Jahn-Teller stabilizations are explicitly considered, such a crossing remains probable. Thus, there remains a large density of charged traps in the center of the gap and a large density of states at the Fermi energy, which have been shown to account for many of the unique experimental properties of the chalcogenide glasses.

4.2 Experimental Studies of a Memory-Type Chalcogenide Glass

We have studied the NMR and transport properties of a chalcogenide glass of composition $Te_{81}\ Ge_{15}\ As_4$. This is an example of a material which

exhibits memory-type switching, as reported by Ovshinsky. We have measured the nuclear magnetic resonance of the Te^{125} nucleus in both the conducting and non-conducting states and have found a 0.1% shift of the resonance line between the two states. The Te^{125} resonance in the conductive state was found to be at precisely the same frequency as in pure crystalline Te, but the spin-lattice relaxation time, T_1, was considerably reduced in the alloy. We have concluded that the conducting state of the alloy contains polycrystalline regions of As-doped Te, the ionized As^- ions being the paramagnetic impurities responsible for the decrease in T_1. The 0.1% shift in the non-conducting state must then represent a chemical shift due to a change in environment of the Te atoms in the glass, necessary if all of the valence requirements of each atom are to be locally satisfied, as is the current model for covalent amorphous semiconductors.

We have also measured the dc conductivity from 4°K to 300°K, the ac conductivity at room temperature up to 150kHz, the ac Hall effect from 77°K to 300°K, and the magnetoresistance at 1.6°K up to 140 k Oe of the conducting state of $Te_{81}\ Ge_{15}\ As_4$. The dc conductivity measurements showed no carrier freeze-out occurs down to 4°K evidence for the semimetallic nature of the state. The Hall experiments showed a temperature-independent carrier concentration, in agreement with this interputation, and a room temperature mobility of 85 cm^2/V-sec. The ac conductivity results were typical of band like conduction in an inhomogeneous material, and the magnetoresistance indicated a two band model is applicable. All of these results are consistent with thermally activated memory type switching being caused by a phase separation of the material into Te-rich and GeTe-rich phases, simultaneously accompanied by the crystallization of highly As-doped Te. Some tentative conclusions regarding field-induced memory switching can also be reached.

5.0 Band Structure and Electrical Properties of Low-Mobility Materials (ARPA, ONR)

5.1 Band Structure of Magnetic Semiconductors

Magnetic semiconductors, such as transition-metal and rare-earth compounds, are generally characterized by a primarily localized optical spectrum, but a band like conductivity. The localized nature of the optical spectrum, even in the case of pure, stoichiometric single crystals must result from the localization of electrons by the intraatomic Coulomb repulsion. This is a correlation effect, neglected in elementary band-structure calculations. In all rare earth compounds and many 3d transition metal compounds, it is a better

approximation to take the 4f or 3d electrons as being in the ionic limit, or completely shielded from the effects of ions other than the one on which they are localized. Using such an approach, we have calculated the electronic and optical energy band structure of pure and Li-doped NiO. The results agree very well with the experimental observations. Furthermore, the somewhat surprising result is obtained that doping NiO with Li or producing a stoichiometric excess of oxygen leads to an effective raising of the oxygen 2p band from far below the Fermi energy, E_F, to about 0.5 eV below E_F. This effect leads to the predominance of 2p holes in the measured electrical conductivity above 150°K, a conclusion which was first made empirically.

5.2 Narrow Energy-Band Theory

An expression for the electrical conductivity of doped or non-stoichiometric Mott insulators has been derived in the limit of strong localization. This expression, based on the Hubbard Hamiltonian, has been applied to Li-doped NiO, and corroborates the conclusion that the 3d band contribution to dc conductivity is experimentally unobservable at all temperatures in this material. It can also be seen how bound-polaron hopping in the 3d band can dominate the ac conductivity at low temperatures and high frequencies.

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II. SUPERCONDUCTIVITY THEORY

Faculty:

Leonard W. Gruenberg, Assistant Professor, Electrical Engineering

Sponsorship:

Office of Naval Research, NONR 3963(16) DSR 74611

Advanced Research Projects Agency SD-90 DSR 75118

Research Report

1.0 The Effect of Magnetic Fields on the Superconducting Transition Region

With the aid of thermodynamic fluctuation theory and a time-dependent Ginzburg-Landau equation, we have studies the behavior of the conductivity of a superconductor in the mixed state as a function of magnetic field and temperature. Near the critical point (H_{c2}, T), fluctuations play an important role and lead to a conductivity which varies as $|H-H_{c2}|^{-\frac{1}{2}}$ for a bulk Type II superconductor and as $|H-H_{c2}|^{-1}$ for a thin film in a perpendicular field. This leads to a temperature-dependent dip in the total resistance R(H) at $H = H_{c2}$. Thus, fluctuations may sometimes be the cause of the peak and dip in flux-flow resistance which is often observed in the mixed state near H_{c2}. A detailed experimental study of the temperature dependence of the width of the dip and comparison with our theory is desirable.

We believe that the conductivity must remain finite at H_{c2} and our present efforts are devoted to including non-linear effects which are important very close to H_{c2}.

2.0 Superconductivity in Very Thin Films and Whiskers

It has been rigorously proved that many phase transitions which occur in three dimensional systems cannot take place in a strictly one or two dimensional system. However, molecular-field theory does not distinguish between one, two, and three dimensions, and is thus inadequate in the study of small systems.

We have developed a phenomenological generalization of molecular field theory which takes into account non-linear fluctuation effects in the simplest self-consistent manner. When applied to superconductors, the theory agrees

with the exact theorems on one and two dimensional systems, and with molecular field theory (except in the critical region) for three dimensional systems. The theory has had some success in explaining resistive transition data on very thin aluminum films. However, when applied to magnetic systems, it does not agree with Onsager's work on the two dimension Ising model. We are presently making several refinements which we hope will improve our model.

Publications:

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III. SEMICONDUCTOR MATERIALS AND DEVICES

Faculty:

R. B. Adler, Professor, Electrical Engineering
R. H. Rediker, Professor, Electrical Engineering
A. C. Smith, Professor, Electrical Engineering
R. D. Thornton, Professor, Electrical Engineering
L. L. Chang, Associate Professor, Electrical Engineering
B. D. Wedlock, Associate Professor, Electrical Engineering
F. O. Arntz, Assistant Professor, Electrical Engineering
J. S. Moore, Assistant Professor, Electrical Engineering
S. D. Senturia, Assistant Professor, Electrical Engineering
D. L. Smythe, Assistant Professor, Electrical Engineering
J. N. Walpole, Assistant Professor, Electrical Engineering
W. H. Berninger, Instructor and Graduate Student, Electrical Engineering

Research Staff:

Dr. F. Ruedenauer, Research Associate, Electrical Engineering

Students:

M. S. Adler, NSF Fellow, Electrical Engineering
R. A. Blanchard, Teaching Assistant, Electrical Engineering
W. S. Brown, NSF Fellow, Electrical Engineering
W. W. Carson, Research Assistant, Electrical Engineering
C. J. Dillon, Graduate Student, Electrical Engineering
C. G. Fonstad, Jr., NSF Fellow, Electrical Engineering
L. Goodman, Research Assistant, Electrical Engineering
R. L. Guldi, NSF Fellow, Electrical Engineering
A. Hartman, Research Assistant, Electrical Engineering
C. R. Hewes, Research Assistant, Electrical Engineering
B. P. Kraemer, Undergraduate Student, Electrical Engineering
R. Lafond, Undergraduate Student, Electrical Engineering
L. S. Loeb, Undergraduate Student, Electrical Engineering
B. P. Mathur, Research Assistant, Electrical Engineering
S. Matsuka, Graduate Student, Electrical Engineering
M. J. McNutt, Undergraduate Student, Electrical Engineering
J. A. Murphy, Undergraduate Student, Electrical Engineering
E. Prahl, Teaching Assistant, Electrical Engineering
D. Reinhard, Teaching Assistant, Electrical Engineering

H. St. Onge, Research Assistant, Electrical Engineering
R. Siegel, Research Assistant, Electrical Engineering
J. R. Smith, Undergraduate Student, Electrical Engineering
J. F. Womac, Research Assistant, Electrical Engineering
R. Van Brunt, Undergraduate Student, Electrical Engineering
W. Yorsz, Undergraduate Student, Electrical Engineering

Support Staff:

Dorothy Chapman, Technician, Electrical Engineering
T. Colozzi, Engineering Assistant, Electrical Engineering
R. W. Kelley, Technician, Electrical Engineering
J. Walsh, Technician, Electrical Engineering
C. J. Yankowski, Student Technician, Electrical Engineering
G. S. Shawnessy, Instrument Maker, Electrical Engineering
Jarmilia Z. Hrbek, Secretary (part time) Electrical Engineering
Berylee Schutz, Secretary (part time) Electrical Engineering

Personnel who have left:

J. M. Borky, (to Armed Services)
R. Broderson, (to Theory Group, M.I.T.)
L. L. Chang, Associate Professor (to IBM)
R. J. Finke, (to industry)
D. Fisher, (to industry)
W. Gajda, (to Notre Dame)
C. R. Grant, Engineering Assistant, Electrical Engineering, (to Lincoln Lab)
B. P. Kraemer, (Graduated)
L. S. Loeb, (to Harvard Business School)
S. Matsuka, (to Hitachi, industry of Japan)
M. J. McNutt, (to University of Illinois)
Wm. Pitkin, (to Polaroid Corp.)
R. M. Refowitz, (Graduated)
J. R. Smith, (to Hughes Aircraft, Fullerton, California)
R. Solomon, (to General Radio)
S. M. Spitzer, (to Materials Group, M.I.T.)
R. Van Brunt, (to Hewlett-Packard Co.)
R. White, (to United Aircraft Co.)

Degrees Granted:

J. M. Borky, S. M. and E. E., Electrical Engineering, May 1969
W. S. Brown, S. M. and E. E., Electrical Engineering, February 1969
C. J. Dillon, E. E., Electrical Engineering, September 1969
B. P. Kraemer, B. S., Electrical Engineering, September 1969

R. J. Lafond, B. S., Electrical Engineering, June 1969

M. J. McNutt, B. S., Electrical Engineering, June 1969

J. R. Smith, B. S., Electrical Engineering, June 1969

R. Van Brunt, B. S., Electrical Engineering, June 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75112, 75115

Office of Naval Research, NOOO 14-67-A-0204-0010, DSR 70421;
NOOO 14-67-A-0204-0029, DSR 71388

Air Force Office of Scientific Research, AFOSR-68-1571, DSR 71013

U. S. Department of Transportation, C-85-65, DSR 76104

National Aeronatics & Space Administration - Electronics Research Center, NgR22-009-234, DSR 70574

M.I.T. Sloan Fund for Basic Research

M.I.T. Lincoln Laboratory

NSF Educational Equipment Grant, DSR 11444

Sylvania Fellowship

NSF Fellows

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 associated technology. Our efforts therefore span the range from investigations 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 Differential Optical Absorption and Reflection

1.1 Optically Pumped Absorption in Cadmium Sulfide

Personnel: Professors F. O. Arntz, R. B. Adler; L. Goodman

Sponsorship: Advanced Research Projects Agency

Measurements of changes in absorption at sub-gap energies due to radiative pumping at energies in the vicinity of the band gap have been performed in Cadmium Sulfide crystals. These measurements have been performed at temperatures of 77°K and 300°K and have been correlated with photoconductivity results acquired on the same crystals. The pumped absorption measurements have proven more time consuming than anticipated, but they have provided a fund of energy-resolved spectra unobtainable with techniques previously employed in the study of trapping kinetics and recombination in II-VI compounds. The results support the conclusion that native defects rather than copper impurities account for recombination in Cadmium Sulfide.

1.2 Electro-Reflection Studies of Mixed Lead-Tin-Telluride Crystals

Personnel: Professor F. O. Arntz; C. J. Dillon

Sponsorship: Advanced Research Projects Agency; Sylvania Corp.

Electro-Reflection of mixed Lead-Tin-Telluride crystals has been

studied using an electrolytic cell technique for the generation of the electric field in the vicinity of the reflecting surface. In most samples the change in reflectivity proved to be simply proportional to the total reflectivity. This was first thought to indicate a problem with the instrumentation, but substantial variation of the proportionality constant with D.C. bias leads to the conclusion that the effect is a legitimate property of the sample-cell combination. Such a result was not observed in a transparent metal - solid insulator - semiconductor sandwich configuration, however.

Fine structure was observed in studies of a few of the more resistive mixed crystals. Two observed peaks are related to peaks previously reported in the electroreflection of pure Lead Telluride, but two peaks in the 1.2 to 1.4 electron volt range are unique to $Pb_xSn_{1-x}Te$. (see Theses).

2.0 Interaction of Successive Diffusions

2.1 Phosphorus and Boron in Si

Personnel: Professor R. B. Adler; E. Prahl

Sponsorship: Advanced Research Projects Agency

The effect of a second diffusion in "enhancing" or "retarding" the diffusion of the first one in a variety of sequential multiple-diffusion process for integrated-circuit planar transistor fabrication has been under study for some years, here and elsewhere. For the most common elements Boron and Phosphorous in Silicon, the effects are especially complicated.

We have found evidence that the "retardation" effect observed with heavily doped bases in pnp transistor-like structures does not develop during the cooling time. Our model for what does happen in those cases suggests that the more common "enhancement" effects observed by us and by others in a number of different structures with less heavily doped bases, and in two different crystal orientations, are also not strongly associated with phenomena which occur primarily during cooling.

Relieving the cooling-time constraint leaves open some reasonable choices in explaining the diverse effects which have been observed, whereas attempting to adhere to this constraint makes the coherent modeling of all the processes extremely difficult.

2.2 Arsenic and Gallium in Ge

Personnel: Professor R. B. Adler; B. P. Mathur

Sponsorship: Advanced Research Projects Agency

The experimental work is proceeding slowly; staining methods for close junctions are now in hand, and masking against As is available. Slices with p-n junctions in them have been supplied kindly by IBM, made by diffusing Ga "bases" into Sb-doped "collector" wafers (lightly doped). We are ready to add As "emitters".

A good deal of study has gone into various theories of bulk interaction phenomena such as electric-field enhancement, vacancy-flux interactions, "chemical-pump" effects etc. These mechanisms must be considered seriously in connection with diffusions carried out at low temperatures, where the elastic limit of the host crystal is relatively high and the Debeye length for screening of impurity charges by mobile carriers is relatively long.

3.0 Physical Effects and X-ray Topographic Evaluation of Interface Strain from Passivating Layers on Silicon

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

Publications on these subjects are still in preparation.

4.0 Nuclear Magnetic Resonance in Solids

Personnel: Professors R. B. Adler, S. D. Senturia, A. C. Smith; M. S. Adler, C. R. Hewes, R. Siegel, B. P. Kraemer, J. A. Murphy, W. Yorsz, C. J. Yankowski

Sponsorship: Office of Naval Research

The research programs reported on below are a continuation of our work on lead salt compounds; the ferroelectric mixed crystal system, sodium potassium tantalate; and most recently, amorphous semiconductors. We seek, using nuclear magnetic resonance and other methods, to extend the fundamental understanding of the electronic structure and electrical properties of these materials.

4.1 Knight Shift in Lead Telluride

Work has continued on the annealing and characterization of good quality lead telluride samples with various carrier concentrations. Both single-zone annealing and two-zone annealing techniques have been used. The effect of powdering on the carrier concentration and the Knight shift has been studied, and will be reported shortly. In each sample, measurements of the Knight shift of the Pb^{207} and Te^{125} nuclei have been made as functions of temperature between 77°K and 300°K. The first major report on this work, including the theory of the Knight shift in the lead salts and a current report of experimental findings, is in the final stages of preparation (C. R. Hewes).

4.2 Knight Shift in (PbSn)Te alloys

Samples have been obtained over a wide range of lead-tin fractions, and preliminary measurements of the Pb^{207}, Te^{125}, and Sn^{119} nuclear resonances have been made as functions of temperature between 77°K and 300°K. Separation of the chemical and Knight shifts requires samples over a wide range of carrier concentrations, and we have begun annealing samples in order to vary the carrier concentrations. Present interest is centered in the range 40% - 60% Pb fraction, where phenomena related to the band crossing are expected to be seen (M. S. Adler).

4.3 NMR in Ferroelectric $Na_xK_{1-x}TaO_3$

After preliminary measurements on the Na^{23} and Ta^{181} nuclear resonances in several non-polar samples, work was begun on the design of a temperature control system for use between liquid helium and liquid nitrogen temperatures. The design of this cryostat is nearly complete, and measurements in the ordered state will follow (R. Siegel).

4.4 NMR Instrumentation

Sensitivity measurements have been made on the nuvistorized marginal oscillator spectrometer designed by Mr. Hewes and Mr. Adler. The resulting data are being compared with a theoretical model of spectrometer sensitivity (M. S. Adler, W. Yorsz).

Investigations into the reduction of nuclear resonance thermometry techniques to simple practice have begun. A literature search for possible

thermometric materials has been carried out preparatory to the design of a semi-automatic high precision digital thermometer (J. A. Murphy).

4.5 Studies of Amorphous Semiconductors

A brief study was made of the Te^{125} nuclear resonance in the two states of a memory-type chalcogenide glass. A 0.1% chemical shift between the conducting and non-conducting states was interpreted in terms of a structure change between the two states (C. R. Hewes).

Transport measurements on the same chalcogenide glass have been carried out. Included in these are the Hall coefficient and resistivity between 77°K and 300°K, and the frequency dependence of the conductivity to 150KHz at room temperature (C. R. Hewes, B. P. Kraemer).

5.0 Microelectronics

5.1 Silicon Device Technology

Personnel: Professor D. L. Smythe; D. Chapman

Sponsorship: Advanced Research Projects Agency

The objective of this program is to increase our understanding of the various silicon device fabrication processes. Three separate studies have been undertaken; 1) Simultaneous fabrication of unipolar and bipolar transistors, 2) Oxide masking during long diffusions, and 3) Silicon dioxide growth rate in wet oxygen.

The theoretical and experimental study of transistor fabrication has shown that double-diffused p-channel field effect transistors and npn transistors can be fabricated in the same wafer using the same two diffusion cycles. The resulting device characteristics, however, leave much to be desired. The JFET has low gain, high pinch-off voltage, and low breakdown voltage; the bipolar transistor has high gain and low punch-through voltage. A computer program has been written and experimentally verified to calculate JFET pinch-off voltage from the diffusion profiles.

Long impurity redistribution (drive-in) diffusions have resulted in an apparent failure of the silicon dioxide masking capability. An experiment has been performed which shows that the reason for this masking failure is the occurrence of surface diffusion along the $Si\text{-}SiO_2$ interface, probably caused by strain in the lattice.

By modifying the single-oxidant theory for oxide growth rate, a general relationship has been derived for the thermal oxidation of silicon by wet oxygen. Experiments to check this relationship are in progress.

6.0 Electric Propulsion

Personnel: Professor R. D. Thornton; W. S. Brown, S. Marshall, R. Van Brunt, D. Saar, W. W. Carson, S. Matsuka

Sponsorship: U. S. Department of Transportation

Mr. Brown completed an MS Thesis "Electronic Commutation for a Direct Current Machine". He successfully operated a rotating field, permanent-magnet machine as a motor, using SCR switching and transistor-transformer commutation. The commutation scheme seemed to be well suited for a machine with a relatively large number of phases (in this case, 12), but motor speed was limited by the turn-off time of the SCR's. A new machine with electromagnetic field and a different position sensing scheme is being explored. Mr. Marshall continued work on the linear synchronous motor with particular emphasis on design considerations for both high speed trains and lower speed automotive-type vehicles. Mr. Saar constructed a new type of two-phase chopper which appears to have high power capability with simplified commutation and lower ripple current in the load. Mr. Van Brunt completed work on a transistor chopper which used many transistors in parallel instead of an SCR. Mr. Matsuka did a preliminary theoretical study of possible ways of modeling SCR's during the transient turn-on condition.

The MIT electric car was converted into a hybrid car in order to provide a convenient test facility for electric propulsion systems.

7.0 High Power Solid State Devices

Personnel: Professor R. D. Thornton; J. M. Borky, R. Blanchard

Sponsorship: National Aeronautics and Space Administration; Advanced Research Projects Agency

Mr. Borky completed an MS Thesis "Use of a Thermal Feedback Stabilizing Mechanism in Power Transistors". He was able to fabricate devices which incorporated negative thermal feedback, but was unable to adequately test the devices. R. Blanchard has designed a new set of device

masks which corrected for problems identified by M. Borky and which allow more complete testing. He plans to fabricate these devices with particular attention to experimental measurements of the improvement in second breakdown characteristics. Other work will explore the extension of these ideas to gate-turn-off four layer devices.

8.0 Study of Basic Device Parameters in the Lead Salts

Personnel: R. H. Rediker, L. L. Chang, J. N. Walpole; R. Guldi, H. St. Onge

Sponsorship: Office of Naval Research, Advanced Research Projects Agency, National Science Foundation Fellowship

In this research program on lead and lead-tin chalcogenides, four areas of work are under way. These are (1) diffusion and interdiffusion, (2) junction devices and Schottky barriers, (3) excess carrier lifetime studies, and (4) high electric field studies. The principal aim of all four areas is better knowledge of fundamental properties of these materials in order to improve the performance of devices and to make possible new devices.

8.1 Diffusion and Interdiffusion

Part of the effort in this area is the routine annealing of the lead salts to adjust the deviation from stoichiometry. We are able to control this parameter and thus carrier type and concentration over a wide range by one- and two-zone annealing. This work is a necessary support to the other programs in which we are involved.

In addition to preparing materials for the other areas, we have in close collaboration with A. R. Calawa of Lincoln Laboratory made a study of the interdiffusion process itself; that is, the process through which the deviation from stoichiometry changes. This work has been a theoretical and experimental investigation of interdiffusion using the p-n junction depth

technique in PbSe. The theory seems to explain the experimental behavior quite well and makes an important contribution to the understanding of both p-n junction device fabrication and annealing work as well.

We have also begun radioactive tracer diffusion work in PbSe using a radioactive selenium isotope. This work will help to establish a more complete model for the diffusion processes and the defect mechanisms in PbSe.

8.2 Junction Devices and Schottky Barriers

We have in close collaboration with K. W. Nill of Lincoln Laboratory fabricated Schottky barriers by evaporation of In, Pb, Sn and Au on n and p-type samples of PbTe and $Pb_{1-x}Sn_xTe$ for x up to 0.30. Most of the devices have been In and Pb on p-type material. Two areas of interest are involved: (a) For low concentration substrates ($<10^{18}cm^{-3}$) good rectification can be obtained with high junction impedances. This result is of interest for possible applications with photovoltaic detectors and for studying the surface properties of lead salts, (b) For high concentrations, the devices show significant tunneling and have been studied by the second-derivative of the current-voltage characteristic for information on the tunneling structure. The tunneling structure has given us the energies of the longitudinal optical phonons in the mixed crystals and we have also seen structure which may be due to the surface plasmon.

8.3 Excess Carrier Lifetime Studies

For the lifetime program, we have been studying the time evolution of photoluminescence from both PbSe and PbTe samples which are 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. We have also measured the branching ratio, defined as the ratio of total lifetime to the radiative lifetime, from the absolute amount of the photoluminescence for different samples of PbSe and PbTe as a function of temperature.

8.4 High Field Conduction Processes

We are investigating two regions of the field-dependent conductivity for homogeneous bulk samples of the Pb salts. These are the hot-electron region where the velocity distribution of the carriers is significantly perturbed from a thermal one and the avalanche multiplication region in which the density of carriers increases by ionization across the energy gap. The experimental observation of these effects without sample heating has been made possible by the development of techniques to produce extremely small samples and by developing pulse techniques to apply pulses with durations of the order of nanoseconds to these samples.

In the fabrication of the samples, ohmic contacts are made to the end portions of rectangular parallelepipeds of PbSe of dimensions typically 0.04 cm x 0.04 cm x 0.25 cm. The center portion of the bar is subsequently etched down to desired dimensions of typically 0.005 cm x 0.005 cm x 0.04 cm. The structure has the present drawback that because the etched cross section of the active area is not constant, it is relatively difficult to reduce the experimentally obtained current-voltage (I-V) characteristics to velocity-electric field (v-E) characteristics. In the results presented below we feel the absolute values obtained for v and E are accurate to 30 percent.

We have seen drift velocity saturation in both n- and p-type PbSe at 77°K, and have for the n-type PbSe seen evidence of

avalanche multiplication. For the samples investigated, the velocity tends to saturate for the p-type PbSe at 1.5×10^7 cm/sec. at 77°K and 1.8×10^7 cm/sec. at 4.2°K and for the n-type PbSe at 2.5×10^7 cm/sec. at 77°K and 2.7×10^7 cm/sec. at 4.2°K, and for n-type PbSe at 77°K avalanche multiplication begins at about 2500 volts/cm.

9.0 Photoluminescence and Photoconductivity in Semiconductors

Personnel: R. H. Rediker, J. S. Moore; A. Hartman

Sponsorship: Air Force Office of Scientific Research

The goal of this program is the study of photoluminescence and photoconductivity in both direct and indirect-gap semiconductors, and of ways to control these phenomena.

Negative photoconductivity in deep-level compensated silicon is being studied. The basic mechanism giving rise to negative photoconductivity in silicon is an optically induced rearrangement of charge on acceptor centers having two energy levels near the center of the forbidden band. After the charge rearrangement, the effective electron capture cross section is increased; hence there is a decrease in the density of conduction band electrons and a decrease in conductivity.

Equal rise and decay times for negative photoconductivity predicted by this mechanism are not observed. Typical rise and decay times are of the order of 10 msec. but the rise time is always less than the decay time by upwards of a factor of two. As the photon energy of the illuminating source approaches the bandgap energy, the time dependence of the amplitude of the conductivity becomes quite complicated. Theoretical models involving excited states of deep levels are being developed which show promise of being able to explain most of our observations.

Further experiments are under way to check these models.

With the intention of modulating the photoluminescence in silicon through the generation of momentum conserving phonons, intrinsic photoluminescence has been measured in high resistivity crystals. During the luminescence measurements, the sample is immersed in liquid helium which has been pumped below the λ point. The spectral lines observed correspond to radiative recombination from the excitonic molecule complex with the emission of momentum conserving TO and TA phonons as well as recombination from the free and bound exciton complexes and also with the emission of momentum conserving TO phonons.

Attempts to modulate the photoluminescence through the generation of TO momentum conserving phonons at a tunnel diode in the luminescent crystal have resulted in a decrease in the luminescence associated with the excitonic molecules. This is presumably due to the annihilation of the excitonic molecule complex through scattering with acoustic phonon generated at the tunnel diode. The absence of modulation of the photoluminescence due to the momentum conserving phonons indicates that the mean free path for such phonons is less than the 100 μm between the active area of the tunnel diode and the surface being optically pumped. Assuming a group velocity for these phonons of 10^4 cm/sec. their lifetime would be less than 10^{-6} sec.

Experiments are now under way to observe enhanced band edge absorption caused by the generation of momentum conserving phonons as well as high energy acoustic phonons at a tunnel diode. In this case the incident light will penetrate the silicon and reach the tunnel junction where the phonons are being generated and should make possible the detection of phonons with shorter lifetime than 10^{-6} sec. without requiring a thinner

base than presently used.

In direct-gap semiconductors, the field control of luminescence is being studied. Silicon nitride has been used as an insulating layer on GaAs through which an electric field can be applied to the surface of the GaAs to modulate the luminescent intensity. The 20 percent modulation of luminescent intensity which has been achieved has been explained by the modulation of surface recombination velocity of GaAs by the applied electric field.

10.0 Study of Stannic Oxide as a High Temperature Semiconductor

Personnel: R. H. Rediker; A Linz; C. Fonstad

Sponsorship: Air Force Office of Scientific Research, Advanced Research Projects Agency, National Science Foundation Fellowship

Single crystals of stannic oxide, SnO_2, of higher purity and with higher Hall mobility than any previously reported have been grown from the vapor using the reaction

$$SnCl_4+2H_2+O_2 \overset{\Delta}{\rightleftarrows} SnO_2+4HCl$$

at 1250°C and 10 Torr. The stannic chloride is obtained from the reaction

$$Sn+2Cl_2 \rightleftarrows SnCl_4+\Delta$$

which is performed in an external reactor and electrical doping is achieved by adding the desired dopant materials to tin charges in parallel doping reactors. Undoped crystals of 6×10^5 ohm-cm resistivity at 300°K, and antimony-doped n-type crystals with resistivity, carrier concentration, and mobility respectively of 0.1 ohm-cm, 4×10^{17} cm^{-3}, and 160 cm^2/V-sec at 300°K and of 0.1 ohm-cm, 6×10^{16} cm^{-3}, and 1200 cm^2/V-sec at 77°K have been grown.

In addition to the electrical measurements, x-ray and spec-

trochemical analyses have been made. Laue x-ray photographs, taken mainly for purposes of orienting crystals, show a large number of sharp spots indicating good crystal quality. Spectrochemical analysis of crystals indicates less than 10 ppm Si and less than 1 ppm of Ca, Cu, and Fe. No other elements were found except for the dopants in doped crystals, but the analysis technique used cannot detect the presence of chlorine so its existence cannot detect the presence of chlorine so its existence cannot be discounted.

Undoped crystals are clear and colorless showing no optical distortion in untwinned portions. Antimony-doped Crystals are slightly bluish in color. No change in growth habit is observed when small concentrations of antimony are introduced, and we have successfully grown n-type antimony-doped layers on undoped high resistivity crystals. Growth on seeds is being investigated. Schottky barrier diodes have been fabricated on n-type SnO_2 and are presently being studied.

11.0 Properties of $Al_xGa_{1-x}As$-GaAs Heterojunctions

Personnel: R. H. Rediker; W. H. Berninger; J. F. Womac

Sponsorship: Advanced Research Projects Agency, Air Force Office of Scientific Research

Liquid phase epitaxy has been employed to deposit tin doped layers of $Al_xGa_{1-x}As$ on to the {111B} face of tin-doped GaAs substrates. The layers are 50-100 μm in thickness with interfaces flat to within ± 1 μm over 500 μm. In order to study the properties of the n-n heterojunction so produced and of the deposited layer, photoluminescence has been investigated as a function of the distance in the layer from the heterojunction and the electrical properties of Schottky barriers on the deposited

layer have been investigated. A focussed HeNe laser has been used to excite photoluminescence in angle-lapped samples at room temperature and at 77°K. The variation in the energy of the near bandgap peak as a function of position combined with published data relating energy gap and Al concentration have been used to obtain a profile of the alloy composition in the layer. This profile has also been obtained from the spectrum of the photoresponse of gold Schottky barriers fabricated at various depths in the layer by a successive lapping and gold depositions. In all samples the Al concentration decreases monotonically with distance away from the interface. For the growth conditions used, the Al concentration at the interface has been determined as a function of Al concentration in the solution for $x<0.32$. In particular, $x=80y$ where y is the atomic fraction of Al in the melt.

The net donor impurity concentration in the deposited layer has been determined as a function of distance from the heterojunction from the capacitance-voltage characteristics of arrays of gold Schottky barriers on angle lapped samples. The carrier concentration was found to decrease with increasing distance from the junction. Since the AlGaAs is deposited at lower temperatures as the layer grows, the variation in carrier concentration is in agreement with published data which indicates a decrease in segregation coefficient with decreasing temperature.

The electrical characteristics of the n-n heterojunctions are being investigated as a function of temperature. In particular, these characteristics are being correlated with the bandgap and the impurity density variations determined from the measurements described above to determine the percentage of the energy-gap discontinuity occurring in the conduction band. Present results indicate that for $\Delta E>0.5$eV and impurity densities less

than 10^{17}/cc, the n-n heterojunctions rectify at 300°K. As either ΔE_g is reduced or the impurity density increased to above 10^{18}/cc, the junctions exhibit near linear I-V characteristics at 300°K as expected.

12.0 Ion Implantation

Personnel: F. G. Ruedenauer

Sponsorship: NASA (MIT Center for Space Research), Lincoln Laboratory

An MIT ion implantation facility has been proposed as a joint program of the Solid State Device Research Group, the Particle Optics Laboratory, and the High Voltage Research Laboratory. This facility would have unique characteristics which would make possible important studies in the solid state device field and in the general area of materials science, including surface metallurgy.

A Unoplasmatron type gas discharge has been chosen as the ion source and has been adapted for operation at temperatures up to 1500°K. Consequently, it is possible to produce μA beams of many metals as well as of gases. We have produced with the sources that have been built μA beams of argon, helium, hydrogen, lead, and gallium.

The first model of the high temperature Unoplasmatron was delivered to Lincoln Lab for use in their 400 KeV Van de Graaf positive ion accelerator.

The main features of the stigmatic double focussing mass analyzer stage which has been designed are a new high transmission sector magnet and a spherical electrostatic condensor resulting in a compact low weight design. Source and analyzer will fit into the inside of a 22" long section of the 20" diameter high-

voltage terminal of the proposed Van de Graff machine and make it a convenient and compact source of monoelemental and in most cases even monoisotopic high energy heavy ions.

13.0 Theory of Conduction in Metal-Insulator-Semiconductor Tunnel Junctions.

Personnel: L. L. Chang, J. S. Moore

Sponsorship: Advanced Research Projects Agency, Air Force Office of Scientific Research

A theory has been developed for the current-voltage and conductance-voltage characteristics in metal-insulator-degenerate semiconductor tunnel junctions. By taking into account the non-parabolic momentum in the insulator, the analysis applies to both n and p type semiconductors. It is found that the current may either increase monotonically as a function of voltage or may exhibit a maximum at a voltage less than the Fermi potential of the semiconductor. The conductance always exhibits a minimum at a voltage equal to or less than the Fermi energy and an additional pair of extrema may exist. The criteria for the various cases have been established in terms of a set of reduced parameters of the junction. The effect of nonequal masses in the semiconductor and the insulator have also considered and shown to be important in determining the different shapes of the characteristics.

Theses:

J. M. Borky, "Use of a Thermal Feedback Stabilizing Mechanism in Power Transistors", S. M. and E. E. Thesis, Department of Electrical Engineering, May 1969.

W. S. Brown, "Electronic Commutation for a Direct Current Machine", S. M. and E. E. Thesis, Department of Electrical Engineering, February 1969.

C. D. Dillon, "Electro-Optic Studies of Lead-Tin Telluride", E. E. Thesis, Department of Electrical Engineering, September 1969.

B. P. Kraemer, "Frequency Dependence of the Conductivity of a Memory-Type Chalcogenide Glass", S. B. Thesis, Department of Chemistry, September 1969.

R. L. Lafond, "Surface State Densities in Silicon Nitride--Gallium Arsenide Structures," S. B. Thesis, Department of Electrical Engineering, June 1969.

M. J. McNutt, "Construction of a Direct-Plotting Inverse Doping Profiler for Semiconductors", S. B. Thesis, Department of Electrical Engineering, June 1969.

J. R. Smith, "A Study of Inclusions in Lead Salt Crystals", S. B. Thesis, Department of Electrical Engineering, June 1969.

R. Van Brunt, "Transistorized Speed Controller For Semiconductor Commutated Motor", S. B. Thesis, Department of Electrical Engineering, June 1969.

Publications:

R. H. Rediker, "Semiconductor Lasers: Still at the Temperature Barrier", Laser Focus 5, 40, March 1969.

L. L. Chang, "Effect of Nonparabolic Momentum on Fowler-Nordheim Tunneling Through an Insulator", Phys. Letters 29A, 125, 1969.

C. G. Fonstad, A. Linz, and R. H. Rediker, "Vapor Phase Growth of Stannic Oxide Single Crystals", Jour. Electrochem. Soc. 116, 1269, 1969.

L. L. Chang and J. S. Moore, "Generalized Current and Conductance Extrema in Metal-Insulator-Semiconductor Tunnel Junctions", Jour. Appl. Phys. (to be published).

R. W. Brodersen, J. N. Walpole, and A. R. Calawa, "Interdiffusion in PbSe", Jour. Appl. Phys. (to be published).

M. S. Adler and S. D. Senturia, "Sensitivity Measurements of Nuclear Magnetic Resonance Spectrometers", Rev. Sci. Instr., November 1969 (to be published).

S. D. Senturia, C. R. Hewes, and D. Adler, "NMR Study of a Memory-Type Amorphous Semiconductor", Jour. Appl. Phys. (to be published).

Electric Car Session, NEREM, November 1968:

W. S. Brown, "A Lightweight Motor for an Electric Car", 1968 NEREM Record, November 1968.

W. W. Carson, "Changing Facilities for the M.I.T. Electric Car", 1968 NEREM Record, November 1968.

C. A. Kaminski, Jr., "Instrumentation and Controls for the M.I.T. Electric Car", 1968 NEREM Record, November 1968.

L. S. Loeb, "The Electric Car - A Systems Approach", 1968 NEREM Record, November 1968.

R. C. Van Brunt, "Speed Control of the M.I.T. Electric Car", 1968 NEREM Record, November 1968.

Papers Presented at Meetings:

A. C. Smith, S. D. Senturia, and C. R. Hewes, "Knight Shift in Partially Degenerate Materials", Bull. Am. Phys. Soc., 14 329, 1969.

S. D. Senturia, A. C. Smith, C. R. Hewes, J. A. Hofmann, and P. L. Sagalyn, "Evidence for a Second Valence Band in Lead Telluride from Knight Shift Measurements", Bull. Am. Phys. Soc. 14 329, 1969.

R. B. Adler and E. Prahl, "Further Studies of Diffusion Interactions Between Phosphorous and Boron Impurities in Silicon", AIME Technical Conference on Defects in Electronic Materials for Devices, August 27, 1969.

L. S. Loeb, "The M.I.T. Electric Car", SAE International Automotive Engineering Congress and Exposition, January 13-17, 1969.

IV. MICROWAVE AND QUANTUM MAGNETICS GROUP

Faculty:

D. J. Epstein, Professor, Electrical Engineering

F. R. Morgenthaler, Professor, Electrical Engineering

W. J. Ince, Assistant Professor, Electrical Engineering

Research Staff:

R. C. Folweiler, Visiting Scientist

Graduate Students:

D. C. Bullock, Research Assistant, Electrical Engineering

H. L. Hu, Research Assistant, Electrical Engineering

J. K. Jao, Research Assistant, Electrical Engineering

A. Platzker, Research Assistant, Electrical Engineering

R. Singer, Research Assistant, Electrical Engineering

L. Tocci, Research Assistant, Electrical Engineering

J. Doane, Graduate Student, Electrical Engineering

Support Staff:

Pauline Alldred, Secretary, Electrical Engineering

Personnel who have left:

R. Nevald, Visiting Assistant Professor, Electrical Engineering (returned to Technical University of Denmark, Lyngby, Denmark)

N. Curland, Research Assistant, Electrical Engineering (now at University of Minnesota, St. Paul, Minn.)

Y. S. Lee, Research Assistant, Electrical Engineering (now at Comsat, Washington, D.C.)

E. Venturini, Graduate Student, Electrical Engineering (now in Military Service)

Degrees Granted:

W. J. Ince, Ph.D., Electrical Engineering, February 1969

Y. S. Lee, E.E., Electrical Engineering, August 1969

N. Curland, S.M., Electrical Engineering, February 1969

K. Kanarek, S.B., Electrical Engineering, June 1969

Sponsorship:

Advanced Research Project Agency SD-90, DSR 75113, 75116

Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, AF (33) 615-3395, DSR 76134

Research Report

1.0 Resonance Losses in Garnets

Personnel: D. J. Epstein, L. Tocci

Valence-exchange losses have been studied in silicon doped single crystals of yttrium-gallium garnet in an effort to determine the functional dependence between the linewidth for uniform precession and the spontaneous magnetization. Our objective of this study was to discover whether we could extract evidence for the presence of an anisotropic background loss of the type proposed by Callen and Pitelli. However, we find that a more consistent interpretation of our data if we assume that the background loss is isotropic.

Clogston assumed in his formulation of the valence-exchange model that only the ground state is significantly populated. However, in the temperature region in which our linewidth studies are being made this assumption is not valid. A correction to the model which takes into account excited state occupancy has been worked out. The revised model improves the agreement between theory and experiment.

2.0 Photomagnetic Effect in Silicon Doped YIG

Personnel: D. J. Epstein, D. Bullock

We have designed and assembled a cryogenic facility which will enable us to make linewidth measurements on Si-YIG, at low temperature, while the sample is illuminated by infra-red radiation near its absorption edge. Previous attempts at low temperature linewidth measurement have been plagued by non-reproducible behavior associated with electrons which have been trapped in metastable states. Illumination will enable us to release these metastable electrons.

Direct evidence for the role played by electrons in the valence-exchange mechanism has been obtained by studying the properties of Schottky barrier diodes fabricated on Si-YIG. When such a diode is back biased we create a

region (the depletion layer) free of electrons, i.e. a region containing only Fe^{3+} ions. In forward bias this region will contain both Fe^{2+} and Fe^{3+} ions and valence-exchange losses can occur. Thus, by turning the depletion layer on and off we change the active volume in which valence-exchange occurs. We have seen this effect in an experiment in which a Schottky barrier diode (gold on Si-YIG) is placed on the end wall of a microwave cavity placed in a d.c. magnetic field. By sinusoidally varying the bias on the diode we are able to modulate the cavity losses. The modulation effect is observed only at magnetic resonance, thereby confirming that we are indeed altering the volume of the sample that is actively contributing to the valence-exchange loss.

3.0 Conductivity in Garnets

Personnel: D. J. Epstein, Y. S. Lee

Measurements of the d.c. conductivity, Seebeck coefficient and Hall effect have been made on doped single crystals of yttrium-iron garnet ($Y_3Fe_{5-\delta}Si_\delta O_{12}$, $0 < \delta < 0.12$) over the temperature range 300 - 550°K. In the ferrimagnetic region (below 550°K) both the ordinary and extraordinary Hall coefficients have been measured. The Hall mobility, calculated from the ordinary Hall constant, is about 0.05 $cm^2\ v^{-1}\ sec^{-1}$ and has only a weak temperature dependence. The conductivity is temperature activated, the activation energy decreasing with increasing doping; for $0.04 < \delta < 0.1$ the activation energy falls from about 0.35 to 0.3 ev. There is no evidence of any discontinuity in conductivity or mobility in passing through the ferrimagnetic - to - paramagnetic phase transformation.

4.0 Thin Film Magnetic Oxides

Personnel: R. Nevald, R.C. Folweiler

Attempts are being made to grow single crystal films of YIG by the method of chemical vapor deposition. We are employing a linear furnace configuration containing three heating zones. Iron chloride vapor is produced in one zone, yttrium chloride in a second and the two reactants are transported into a third zone where, under appropriate conditions, they react in the presence of oxygen and hydrogen to form $Y_3Fe_5O_{12}$ on a suitable substrate. To make the process work, reaction temperatures and flow rates have to be carefully adjusted. At the moment we are still in the adjustment

stage and have not yet succeeded in producing YIG films.

5.0 Magnetic and Elastic Studies of the Antiferromagnet $RbMnF_3$

Personnel: F. R. Morgenthaler; W. J. Ince; A. Platzker

5.1 Coupled Electronic and Nuclear Modes

In his recently completed doctoral thesis W. J. Ince has reported an investigation of the coupling between the antiferromagnetic and Mn^{55} nuclear resonance modes in $RbMnF_3$. Expressions for the electronic and nuclear frequencies have been derived by solving the coupled equations of motion for; (a) a four sublattice model, consisting of two electronic and two nuclear magnetic sublattices; (b) a two sublattice model in which the electron-nuclear interaction is represented by a static anisotropy field. It has been shown that for the electronic modes the differences in the frequencies obtained from the two models are generally small.

On the other hand, only the four sublattice theory predicts the NMR frequencies to good accuracy for applied fields both greater and less than the spin-flop value. The temperature dependence of the appropriate crystal parameters for $RbMnF_3$ were included in the theory, enabling a detailed comparison between theory and experiment to be made in the temperature range where the parallel susceptibility is significant.

Electron - nuclear double resonance experiments with $RbMnF_3$ have been continued. Nuclear saturation was detected as a shift in the applied field for AFMR. The range of pump frequency over which nuclear saturation could be induced was roughly 100 MHz. The measurements have yielded a value of 686.5 MHz for the unpulled hyperfine frequency. The AFMR monitoring frequency in these experiments was in X - band. Further work has been carried out using a monitoring frequency of 23.16 GHz. This has permitted smaller geometry, thereby reducing power requirements and attendant heating effects. Measurements have been made down to a temperature of $1.8^{o}K$, where the longitudinal relaxation rate T_1 was about 200 msec, compared to 55.5 msec at $4.2^{o}K$.

Single crystals of cobalt doped $RbMnF_3$ have been prepared in the Crystal Physics Laboratory by the Czochralski method. Doping concentrations ranged from zero to about 1500 ppm. The influence of the dopant on the crystalline anisotropy constants has been studied via magnetic resonance. It was found from AFMR measurements that the crystalline cubic anisotropy constant K_1 varies in a fairly linear manner with cobalt concentration. There appears

to be little or no increase in K_2. The constant K_1 becomes zero at about 340-ppm cobalt concentration. The computed AFMR and Mn^{55} nuclear mode spectra, taking into account the variation of K_1 due to the presence of the dopant, generally fitted the experimental data very well. This implies that the sublattice magnetizations and the exchange and nuclear hyperfine fields are essentially unaffected by the presence of cobalt, at least for the range of doping concentrations used. Some additional modes were observed which are not predicted by the theory but may be due to local impurity states.

5.2 Phonon and Photon Pumped Spinwaves

Mr. A. Platzker is nearing the completion of his doctoral research involving phonon-and photon-pumped electronic and nuclear spinwaves in $RbMnF_3$.

The excitation of first order spin waves instabilities in an antiferromagnet which may carry a nuclear moment has been critically reexamined. Nuclear, electronic and mixed magnon pairs can be excited by processes which are analogous to the ferromagnetic case. Various geometries of pumping fields are possible and their correct critical values have been derived. Contrary to the assumption of previous authors, we have shown that when photon pumping fields are applied to a flopped antiferromagnet, the uniform precession is always excited and its contribution to the threshold amplitude is significant and can never be neglected. This implies that direct magnon excitation in which the linear susceptibility is negligibly small (parallel pumping) does not exist in an antiferromagnet when the weak dipolar effects are ignored. However, when phonon fields are applied, parallel pumping processes are allowed[1] due to the change in symmetry of the effective magnetoelastic pumping fields. In particular when a longitudinal wave is propagating parallel (or nearly so) to the d.c. sublattice magnetizations the effect of the negligibly small linear susceptibility can be ignored and the process is analogous to parallel pumping in a ferromagnet.

6.0 Frequency and Mode Conversion of Velocity Modulated Magnetoelastic Waves

Personnel: F. R. Morgenthaler; H. L. Hu; J. K. Jao

The frequency of a magnetoelastic wave propagating in a ferrimagnet can be altered by a suitable time variation of the bias magnetic field and the character of the wave can be 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 for microwave ultrasonic devices.

We have carried out the first successful conversion of z-directed spin waves to longitudinal elastic waves (and vice versa) in an axially magnetized (z-axis) single crystal YIG rod. The conversions - carried out at L-band frequencies and room temperature - were controlled by means of temporal and/or spatial magnetic field gradients. They were possible because the symmetry axis of the rod was not along a principal crystallographic direction; the axis was chosen to be in a (100) plane at an angle 22.5° with respect to a <100> direction in order to provide nearly maximum spin-longitudinal elastic wave coupling. At room temperature, the critical longitudinal temporal and spatial field gradients for this geometry are calculated to be respectively 100 oe/μsec/GHz and 150 oe/cm/GHz. In contrast the corresponding critical shear gradients are on the order of 7,400 Oe/μsec/GHz and 19,000 Oe/cm/GHz.

7.0 Coupling of Magnetoelastic and Electromagnetic Waves

Personnel: 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 examined. 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.

J. Doane is nearing completion of a doctoral thesis aimed at improving our understanding of the mechanisms of coupling between electromagnetic energy and magnetoelastic energy in delay lines, with the hope of developing better excitation schemes. During the past year a study has been made of the coupling processes which occur between long-wavelength "magnetostatic waves" and short-wavelength spin waves at turning points in these delay lines. Motivated by a desire to resolve inconsistencies between existing experimental data and their theoretical explanation, this study has required the search of literature in plasma physics and ionospheric radio-wave propagation for techniques. Similar coupling processes occur between transverse electromagnetic waves and longitudinal plasma waves in propagation in radially inhomogeneous plasmas, such as in certain plasma heating schemes. Ordinary successive approximations methods (such as used in magnetoelastic coupling analysis) and WKB methods used in solving coupled mode problems

in inhomogeneous media are not useful here since two reflected waves are generated by one incident wave, and all four quasi-normal modes interact strongly at the turning point. Certain analytical results for single-frequency reflection and conversion coefficients including the effect of loss have been obtained in terms of generalized hypergeometric functions. Further work will probably include numerical computations for comparison.

8.0 Magnetostatic Surface Waves

Personnel: F. R. Morgenthaler

The characteristics of TE surface waves propagating in an obliquely magnetized uniform ferrite medium have been examined -- with special emphasis given to the magnetostatic region of the dispersion relation. It appears that independent control of the propagation and decay constants is possible. In addition, the waves are nonreciprocal in the field displacement sense allowing novel magnetic control to be exercised over them. In particular, it should be possible to vary the depth of penetration of a wave and in fact cause it to switch from one to the other surface of a magnetic substrate. It appears likely that novel couplers, switches, isolators and circulators can be constructed with convenient planar geometries.

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W. J. Ince, "Coupled Antiferromagnetic-Nuclear Magnetic Resonance in $RbMnF_3$", Ph.D. Thesis, Department of Electrical Engineering, February 1969.

Y. S. Lee, "Transport Properties in Doped Single Crystal Yttrium-Iron Garnet", E.E. Thesis, Department of Electrical Engineering, August 1969.

N. Curland, "Magnetoelastic Interaction Studies Using Moveable Fine Wire Excitation", S.M., Department of Electrical Engineering, December 1968.

K. Kanarek, "A Computer Animated Representation of Waves Propagating in Magnetic Crystals", S.B.E.E., Department of Electrical Engineering, June 1969.

Publications:

W. J. Ince and A. Platzker, "Antiferromagnetic Domains in $RbMnF_3$", Phys. Rev. 175, 650 (1968)

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S. M. Rezende and F. R. Morgenthaler, "Magnetoelastic Waves in Time-Varying Magnetic Fields. I. Theory", J. Appl. Phys. 40, 524 (1969)

S. M. Rezende and F. R. Morgenthaler, "Magnetoelastic Waves in Time-Varying Magnetic Fields. II. Experiments", J. Appl. Phys. 40, 537 (1969)

F. R. Morgenthaler, "A Figure of Merit for Magnon-Elevation and Elastic Wave Conversion in YIG", to be published in Proceedings of 1969 Ultrasonics Symposium, Sept. 24 - 26, St. Louis.

F. R. Morgenthaler, S. M. Rezende, H. L. Hu and A. Platzker, "Spin-Longitudinal and Spin-Shear Elastic Wave Conversion in an Axially Magnetized YIG Rod", submitted to Applied Physics Letters.

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magnets", to be published in J. Appl. Phys.

F. R. Morgenthaler, "A Nonreciprocal Magnetostatic Surface Wave With Independent Propagation and Decay Constants", to be published in J. Appl. Phys.

H. L. Hu, S. M. Rezende and F. R. Morgenthaler, "Measurements of Spatial and Temporal Efficiencies for Longitudinal Elastic Wave/Spin Wave Conversion in an Axially Magnetized YIG Rod", to be published in J. Appl. Phys.

V. CRYSTAL PHYSICS AND OPTICAL ELECTRONICS LABORATORY

Faculty

A. Smakula, Professor, Electrical Engineering
D. J. Epstein, Professor, Electrical Engineering
T. G. Davis, Assistant Professor, Electrical Engineering

Research Staff

Dr. A. Linz, Research Associate, Electrical Engineering
J. Kalnajs, Research Physical Chemist, DSR Staff
Dr. D. Gabbe, DSR Staff (part-time)
E. Farrell, DSR Staff
V. Belruss, DSR Staff
Mrs. A. Szorc, DSR Staff (part-time)

Graduate Students

J. T. Carlo, Graduate Student, Electrical Engineering
E. K. Chan, Research Assistant, Electrical Engineering
T. M. Grove, Graduate Student, Electrical Engineering
H. P. Jenssen, Research Assistant, Electrical Engineering
P. C. M. Munasinghe, Research Assistant, Electrical Engineering
R. A. Schaffzin, Teaching Assistant, Electrical Engineering
L. T. Todd, Graduate Student, Electrical Engineering
S. D. Seccombe, Undergraduate Student, Electrical Engineering

Support Staff

R. Mills, Project Technician
A. Vetrovs, Technical Assistant
C. A. Clark, Technician (Northeastern Co-op Student) (part-time)
Mrs. Delphine Radcliffe, Secretary

Personnel who have left

T. M. Grove, Graduate Student - enlisted in United States Air Force
P. C. M. Munasinghe, Research Assistant - returned to Ceylon.
R. A. Schaffzin, Teaching Assistant - now at Fairchild Semiconductor, Inc., California.

Degrees Granted

T. M. Grove, S. B., S. M., Electrical Engineering, December 1968.

P. C. M. Munasinghe, S. M., E. E., Electrical Engineering, September 1969.

R. A. Schaffzin, E. E., Electrical Engineering, September 1969.

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Research Report

1.0 Crystal Growth

Personnel: A. Smakula; A. Linz; J. Kalnajs; D. Gabbe; E. Farrell; V. Belruss; R. Mills; A. Vetrovs; C. A. Clark

1.1 Ferroelectric Crystals

Top-seeded solution growth of ferroelectric crystals has continued where the crystals are required. This has included pure and doped $BaTiO_3$ for conductivity studies and $(K, Na)TaO_3$ and $K(Nb, Ta)O_3$ for Raman scattering and dielectric studies. Top-seeded solution growth of $Bi_4Ti_3O_{12}$, an oxygen octahedra type ferroelectric with a complex layer structure, was not successful. No way of altering the platey habit has been found to date. Top-seeded solution growth of $Gd_2(MoO_3)_4$ was abandoned in favor of Czochralski growth in the high temperature oxide furnace where good quality crystals were obtained. Crystals of barium strontium niobate bronzes have been grown for special studies as thermal and long wavelength optical detectors. Considerable work has also been done on developing crystals of a rare earth titanate bronze structure, but all pure titanate materials have crystallized in the pyrochlore structure to date.

1.2 Germanates

Work on the growth of rare earth doped crystals of $Ba_2MgGe_2O_7$ by top-seeded solution techniques has continued for laser host studies.

Germanate garnets such as $CaY_2Zn_2Ge_3O_{12}$ have also been grown for study as host materials for optically pumped lasers. Other complex germanate and silicate systems are under study.

1.3 High Temperature Oxides

Construction of a high temperature R. F. induction heated Czochralski furnace has been completed and a large number of crystals of $Gd_2(MoO_4)_3$ have been grown. This relatively low melting material (mp 1165°C) has allowed us to perfect growth techniques which are applicable to materials with temperatures in excess of 1500°C while providing the crystals required for research. Flat based reinforced cylindrical crucibles of platinum have been developed for $Gd_2(MoO_4)_3$ and similar crucibles of iridium for higher temperature materials. A quartz tube sealed at each end surrounding the crucible provides a means of viewing the growing crystal while the atmosphere is controlled by the introduction of an appropriate gas. This provides us with a steep radial gradient furnace capable of operating over a wide range of temperatures and controlling atmospheres.

Several problems in growing $Gd_2(MoO_4)_3$ have been overcome. The nonstoichiometry of the feeds and consequent Gd excess crystals was corrected by pre-calcining the feed. Cracking of crystals which occurred on cooling was prevented by annealing the crystals in a wire wound resistance furnace incorporated into the Czochralski system, thus providing in situ annealing. Expansion and the consequent distortion of the crucibles was corrected by surrounding the crucible with a ZrO_2 ceramic jacket which reduced expansion considerably.

Growth of several crystals of olivine (Mg_2SiO_4) by flame fusion has led to an understanding of some techniques of silicate chemistry and crystal growth. A more complex system is represented by the anorthite-wollastonite phase diagram ($CaAl_2Si_2O_8$, $CaSiO_3$, respectively). Initial efforts to grow anorthite by the top-seeded solution method from this system have been encouraging, as evidenced by anorthite nucleation, but glass formation on the seed rod has hampered crystal growth. Growth with natural anorthite seeds and/or the suppression of the glass phase by substitution of Ge for Si should lead to successful growth of anorthite.

Routine growth of crystals supplied on request is continuing. A NiO single crystal six inches in length has been grown, and several spinels doped with Cr^{+3} and Nd^{+3} have been produced, all by the flame fusion technique. Other crystals of the transition metal oxides have been grown for inventory.

Several attempts at the growth of $Bi_4Ti_3O_{12}$ by the Czochralski technique have not proved satisfactory because of the micaceous nature of

$Bi_4Ti_3O_{12}$ and the reactivity of the Bi melt with the platinum crucibles at elevated temperatures.

1.4 Fluorides

1.4.1 Zone Refining

A high vacuum/inert gas zone refiner heated by RF power has been designed. Based on past experience with zone refining, it is expected that oxide impurities and extraneous floating material which appears on the surface of the melt during crystal growth will be completely removed. These two impurities are detrimental to growth of high quality single crystals.

1.4.2 Crystal Growth Furnaces

In cooperation with the Norton Company, one of the laboratory's crystal pullers is being equipped with a vacuum/pressure tight interlock which will enable crystals to be removed from, and seeds to be inserted into, the furnace, without having to shut down the furnace. Several advantages will be realized. The total time required to produce a crystal will be reduced by at least a factor of two. And time lost to shutdowns during those operations designed to prepare the melt surface for seeding will be eliminated. In addition, the time required to replace a seed after accidental loss will be reduced by a factor of two.

1.4.3 Potassium Manganese Fluoride

Crystals of $KMnF_3$ for neutron scattering experiments are being grown. Efforts are being made to reduce strain and mosaic spread by growing a series of crystals, each one nucleated on a seed taken from the most perfect portion of the previous boule.

1.4.4 Rubidium Fluoride

A single crystal of RbF was grown. This material is extraordinarily deliquescent and can be exposed only to a rigorously dry atmosphere.

1.4.5 Lithium Yttrium Fluoride

Many lithium yttrium fluoride crystals doped with numerous rare earths singly and in various combinations have been grown for spectroscopic and laser studies. Neodymium-doped $LiYF_4$ has been grown for laser crystals.

1.4.6 $LiYF_4$:Er, Tm, Ho and $LiYF_4$:Er, Yb, Tm, Ho

Crystals having the above compositions were grown for study as potential 2μ lasers. Er^{3+} doping was about 50% of the total rare earths.

1.4.7 Ultra Purification of Materials

The synthesis of ultra-pure $RbMnF_3$ is being carried out with a view toward characterising the relationship between impurities and the magnetic properties of $RbMnF_3$. Rubidium chloride with a purity of at least 10^2

better than the material which was previously used is now available. An ion exchange process for converting the RbCl to Rb_2CO_3 - necessary for the synthesis of $RbMnF_3$ - is being developed. Purification of the manganese will be done by zone-refining reagent grade $MnCl_2$.

1.5 Growth of Thiospinels

Crystals of $CdIn_2S_4$ were grown by an iodide transport vapor phase technique for investigation as CO_2 laser window materials. Small crystals with the typical spinel octahedral habit were obtained and were of sufficient size for testing. The relatively high free carrier absorption at 10.6 microns precluded their use as CO_2 window materials. Attempts are in progress to obtain larger samples using a Bridgeman technique in sealed quartz crucibles.

2.0 Crystal Research

2.1 Ferroelectric Studies

2.1.1 Raman Scattering in Mixed Crystal Ferroelectrics (T. G. Davis; L. T. Todd)

This project is concerned with investigations of "soft" phonon modes in the ferroelectric mixed crystal systems $(K_xNa_{1-x})TaO_3$ and $K(Ta_xNb_{1-x})O_3$. In the $(K_xNa_{1-x})TaO_3$ system, all the paraelectric-ferroelectric transitions are thermodynamically second-order. In all compositions which undergo transitions we have observed temperature dependence of the ferroelectric mode in the cubic perovskite phase by means of electric-field-induced Raman scattering. At the transition temperature the mode becomes unstable, inducing the transition to a ferroelectric state. At temperatures below the transition, the "soft" phonon mode has been observed by means of conventional Raman spectroscopy. These experiments represent the first observations of well-defined soft modes in the polar phase of a ferroelectric.

Crystals of $(K_xNa_{1-x})TaO_3$ for which $0.5 < x < 0.7$ undergo two phase transitions. The highest temperature one occurs in the region 50^oK - 65^oK; it is a transition from cubic perovskite to a tetragonal ferroelectric phase. An additional transition to a lower symmetry ferroelectric phase occurs in the interval 5^oK to 30^oK. Soft phonons associated with the lower temperature transitions have also been observed.

In the mixed crystal system $K(Ta_xNb_{1-x})O_3$, compositions for which $x \geq 0.8$ undergo second-order ferroelectric transitions, while those for which $x < 0.8$ undergo first-order transitions. Well-defined soft phonon modes have been observed only in those crystals which have second-order transitions. First-order transitions appear to be associated with phonons

which are heavily over-damped. Present studies are concerned with Raman scattering in crystals having compositions near the critical value at which the order of the transition changes.

2.1.2 Semiconducting Ferroelectrics (D. J. Epstein; T. M. Grove)

Barium titanate is a ferroelectric material which normally has a resistivity in excess of 10^9 ohm cm. However, by reduction in hydrogen or by the addition of suitable dopants, it can be made a semiconductor with a room temperature resistivity below 100 ohm cm. In this semiconducting state the resistivity of ceramic barium titanate exhibits an anomalous positive temperature coefficient (PTC) effect in the vicinity of the ferroelectric-to-paraelectric phase transition. The precise origin of this effect has not been established, but it has been suggested that the governing mechanism is a strongly temperature-dependent depletion layer occurring at grain boundary contacts.

We have prepared ceramic samples of barium titanate doped with tantalum and compared their conductive properties with those of single crystals made semiconducting by hydrogen reduction. A large PTC effect was seen in the ceramic samples. Although measurements on the single crystals were plagued by unexplained aging, drift and hysteretic effects, our results to date indicate that PTC behavior does not occur in single crystals, therefore lending support to the grain boundary model.

A detailed investigation of transport properties in doped single crystal barium titanate has been initiated. Conductivity, Hall constant and Seebeck effect will be studied as a function of temperature for various dopants (e.g., tantalum, niobium, cerium) over a range of doping concentrations.

2.1.3 Optical Ferroelectrics (D. J. Epstein; A. Linz; E. F. Farrell; V. Belruss; A. Vetrovs)

Bismuth titanate and gadolinium molybdate are ferroelectric crystals which, because they exhibit a "latched-state" birefringence, are potentially useful as optical gates and memory cells. Attempts to grow suitable crystals of $Bi_4Ti_3O_{12}$ have thus far been unsuccessful. The crystal tends to a micaceous growth habit and we have been unable to alter this tendency in any growth procedure we have tried. Crystals of $Gd_2(MoO_4)_3$ have been grown both by the top-seeded solution and the Czochralski techniques. The latter method is the better one and using it we have grown a number of crystals of good optical quality.

Studies of the electrical, electro-optical and acoustic properties of $Gd_2(MoO_4)_3$ will be undertaken during the forthcoming year.

2.1.4 Electro-optical Deflectors (A. Linz; R. Schaffzin)

Use of $BaTiO_3$ above its Curie temperature as a quadratic electro-optical

deflector was studied. A prototype laser scanner was constructed using prisms of this material and deflections of several tenths of a degree were observed at low frequencies. At higher audio frequencies large losses precluded use of the device due to heating. The theoretical aspects of laser deflection using barium titanate crystal prisms were studied, including prism configuration, angular incidence and temperature and frequency dependence. Techniques needed for crystal preparation were explored and the practicality of the resulting device appeared to be dependent on the quality of the crystal, in particular the high temperature conductivity properties. It was concluded that the high temperature of operation interfered seriously with the efficiency of the device, although it would probably help avoid laser damage due to high light field intensities.

2.2 Optically Pumped Laser Crystal Research

2.2.1 Rare Earth Fluorescence in Barium Magnesium Germanate Crystal and Glass Hosts (A. Linz; P. C. M. Munasinghe)

During the period covered by this report, a thesis on barium magnesium germanate ($Ba_2MgGe_2O_7$) glasses and crystals doped with Nd^{3+} was completed.

Nd^{3+} appears to occupy the Ba^{2+} site in the crystal, but inhomogeneous line broadening in the glass indicates that a variety of sites are available. Beer's law is obeyed for both hosts.

Concentration quenching begins at 0.5 mole % Nd^{3+} doping in the glass, but is not observed in the crystal. This and other results are shown to be consistent with the existence of two resonant energy transfer mechanisms between Nd^{3+} ions. Investigation of impurity quenching due to iron yields ~ 20 Å for the range of the neodymium-iron interaction, based on a simple model. The Stark splittings of the main Nd^{3+} fluorescent levels in the crystal have been determined and various anomalies in the spectroscopic and lifetime data are examined. Some work is still going on to further interpret the results, especially in terms of crystal field theory in glasses, and we also hope to study other rare earth ions and energy transfer systems in both the crystals and the glasses, especially with reference to changes taking place during the devitrification of the glasses.

2.2.2 Fluorescence of Nd^{3+} in Complex Germanate Garnets (A. Linz; E. K. Chan)

A study of a new complex garnet crystal, $CaY_2Zn_2Ge_3O_{12}:Nd^{3+}$ has also been completed during this period. A comparison was made between this material and neodymium-doped YAG, which showed that there is more line broadening in the former, as might be expected in a disordered crystal,

but that also a great deal more of the fluorescent energy comes out in the transition to the ground state at 9400 Å in the complex garnet compared with the amount in YAG. The tendency of this crystal to pronounced cracking after growth is apparently due to a change in stoichiometry, indicated by changes in the x-ray lattice constant during growth. Another garnet system, $Ca_3Y_2Ge_3O_{12}$, is being studied also, since it is a somewhat simpler system. If this germanate analog of the known silicate really exists, it will permit us to study the degree of ordering between calcium and yttrium and yttrium and germanium sites in a somewhat simpler compound. If the compound orders it will provide an octahedral rare earth site with a center of symmetry which would be of considerable interest.

2.2.3 Sensitized Luminescence in Rare Earth Fluorides (A. Linz; H. P. Jenssen; J. T. Carlo)

The investigation of fluoride crystals has been largely concentrated on sensitized luminescence. Since $LiYF_4$ will accept up to 100% substitution of the yttrium with many of the other rare earth elements, a more complete study of sensitized luminescence is possible in this material than in other common laser host crystals such as CaF_2 and YAG. Preliminary results of conversion of near infrared to visible green light utilizing energy transfer from ytterbium to erbium were studied. Transfer from erbium to holmium with thulium as an intermediate is also under investigation to obtain efficient lasers in the 2 micron region. The possibility of pumping such lasers with semiconductor light emitting diodes is also under investigation. Since phonon processes appear to play a large role in the energy transfer process, a new crystalline material, Cs_3YF_6, with a lower energy phonon spectrum compared to $LiYF_4$, is under development. This material is of interest also since it appears to have a rare earth site with a center of symmetry, a relatively uncommon phonomenon among rare earth hosts.

$LiYF_4$ is also being studied in the infrared quantum counter mode as a narrow band imaging detector for near infrared laser radiation.

2.3 Dielectric Investigation of Semiconductors (A. Smakula; A. Szorc)

The discontinuous variation of dielectric properties (κ' and κ'') at low frequencies, below 10^7 Hz, and low temperatures, below 30^oK, which has been discovered in various semiconductors (Ge, Si, GaAs, CdS) and reported previously, has been investigated in more detail on p-type Si doped with B, n-type Si doped with P and compensated Si doped with B and P simultaneously.

It was found that the discontinuity of κ' takes place at different

temperatures for p-type and n-type Si, and it also depends on frequency. The temperature range of strong κ' change lies between 16 and 23°K for Si:B, between 21 and 31°K for Si:P, and between 22 and 44°K for Si:B+P, all for 10^3 Hz. Simultaneously with κ' the κ'' changes and reaches a maximum value at the inflection point of κ'. The temperatures of κ'' maximum are: 21.5, 25.3, and 33.5°K for the same sequence as for κ'. Since no anomalies have been discovered at frequencies above 10^8 Hz, we have to assume that we deal here with thermal ionization of donor and acceptor levels. A strong shift of κ'' maximum of compensated Si to temperatures above that of p-type and n-type indicates an interaction of acceptors and donors. Other p-type and n-type Si crystals are under study.

2.4 Crystals for CO_2 Laser Windows (A. Smakula; J. Kalnajs)

A good window material for CO_2 lasers should have high hardness, high thermal conductivity and low absorption at 10.6 μ. The most important property is the low absorption in the infrared spectral region. The absorption can be caused by the tail of eigenabsorption band, overtone or combination bands, impurities, defects, surface imperfections, surface contaminations and free charge carriers.

Three types of crystals have been studied: thiospinels, III-V semiconducting compounds, and alkali halides. Of the first group, $CdIn_2S_4$ crystals were grown by chemical transport reaction under various conditions but all showed the high absorption (25% per cm) at 10.6 μ, probably caused by the close proximity of the absorption edge (14 μ).

Pure stoichiometric GaSb should have an infrared absorption edge around 18 μ, but our material showed free charge carrier absorption at wavelengths shorter than 10.6 μ. Doping may reduce the free charge carriers, but may introduce absorption from the dopant ions.

The most extensive study was made on alkali halides. The alkali fluorides (KF, RbF and CsF) are too deliquescent and their absorption tail is too close to 10.6 μ. Of the chlorides (NaCl, KCl and RbCl), RbCl is the best. Its absorption at 10.6 μ is 0.093% per cm (the lowest of all known materials). The bromides (KBr and RbBr) are less useful because of their solubility and softness. The absorption of CsI is 0.13% per cm (quite close to RbCl) but the solubility is very high and the hardness low. The spectral position of the infrared absorption edge, purity, and surface contamination are decisive factors for optical properties. For selection of the best crystals, we have, however, to compromise between the optical and mechanical properties.

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T. G. Davis, C. H. Perry, N. E. Tornberg and N. Knable, "Optical Phonons in Mixed Sodium Potassium Tantalum" - published in National Bureau of Standards Special Publications, 1967, No. 301 (Published 1969).

Papers Presented at Meetings

T. G. Davis, "Soft Phonon Modes in the $(K, Na)TaO_3$ Mixed Crystal System",

Invited paper, Ferroelectrics Symposium, American Physical Society Spring Meeting, April 28 - May 1, 1969, Washington D. C.

T. G. Davis, "Soft Phonon Modes in Mixed Crystal Systems (K, Na)TaO_3 and K(Ta, Nb)O_3" - Second International Meeting on Ferroelectricity, September 4 - 9, 1969, Kyoto, Japan.

C. G. Fonstad, A. Linz and R. H. Rediker, "Vapor Phase Growth of Stannic Oxide Single Crystals", ACCG Conference on Crystal Growth, August 11-13, 1969, National Bureau of Standards, Gaithersburg, Maryland.

C. S. Naiman, A. Linz, and E. F. Farrell, "Optical Spectroscopy of Chromium as a Coordination Identifier in Crystal Growth", ACCG Conference on Crystal Growth, August 11-13, 1969, National Bureau of Standards, Gaithersburg, Maryland.

D. R. Gabbe, "Scheelite Structure Fluorides - The Growth of $LiYF_4$:Er, Tm, Ho and $LiYF_4$:Er, Yb, Tm, Ho", ACCG Conference on Crystal Growth, August 11-13, 1969, National Bureau of Standards, Gaithersburg, Maryland.

V. Belruss, A. Linz, and R. C. Folweiler, "Top-Seeded Solution Growth of Complex Germanates", ACCG Conference on Crystal Growth, August 11-13, 1969, National Bureau of Standards, Gaithersburg, Maryland.

A. Linz, "Growth of Perovskite-Type Ferroelectric Crystals" - Invited paper, Ferroelectrics Symposium, Electrochemical Society, Fall Meeting, October 6-11, 1968, Montreal, Canada.

Reports

Semiannual Technical Reports on Contract No. N00014-67-A-0204-0025, "Growth of Thiospinels" for period June 1 through December 31, 1968, and period January 1 through June 30, 1969.

Semiannual Status Reports on Contract No. Nonr-3963(20), "Growth and Study of Certain Perovskite-Structure and Related Laser Host Crystals" for period June 1 through November 30, 1968, and period December 1 through May 31, 1969.

VI. PARTICLE OPTICS LABORATORY

Faculty:

C.K. Crawford, Associate Professor, Electrical Engineering

Research Staff:

F.G. Ruedenauer, Research Associate, Electrical Engineering

Graduate Students:

K.L. Wang, Research Assistant, Electrical Engineering
M.D. Brody, Graduate Student, Electrical Engineering
N.D. Punsky, Graduate Student, Electrical Engineering
T.J. Harris, Graduate Student, Electrical Engineering

Support Staff:

C. Breverman, Undergraduate Student, Electrical Engineering
R.M. Lucash, Undergraduate Student, Physics
Janice M. Oxton, Secretary, Electrical Engineering

Personnel who have left:

A. Shigamoto
L.L. Wischhoefer

Degrees granted:

A. Shigamoto, S.B., Electrical Engineering, June 1969
L.L. Wischhoefer, S.B., Electrical Engineering, June 1969

Sponsorship:

Air Force Materials Laboratory, F33615-68-C-1020, DSR 70653
NASA Electronics Research Center NAS12-679, DSR 71060
Lincoln Laboratory POA-2266, DSR 71232
Sloan Basic Research Fund 27568

Research Report

This laboratory was set up to study low energy charged particle optics, neutral and charged particle beams, and related subjects. Areas of interest include mass spectrometry, scanning electron microscopy, surface effects and high brightness sources of both electrons and ions.

1.0 Surfaces-Solids Mass Spectrometer Facility

Personnel: C.K. Crawford; F.G. Ruedenauer

Sponsorship: Sloan Basic Research Fund 27568

The design and construction of a new mass spectrometer for use both in studying surfaces and in the bulk analysis of solids has been undertaken. The basic design for use in surface studies (measurements of concentration gradients, corrosion layers, semiconductor junctions, and thin films) will be a sputter ion source mass spectrometer equipped with a scanning microfocus primary spot and primary mass analysis. The secondary ion analyzer will be a double focusing mass spectrometer equipped with a feedback stabilized magnetic field and an electron multiplier ion detection system.

The instrument is being designed to allow the modular replacement of the ion source and other major components, and to permit the modular addition of other experiments to be conducted simultaneously with the ion microprobe analysis. The instrument is designed to operate completely in ultra-high vacuum. Much of the instrument will be constructed from commercially available components.

A major departure from previous microprobe design will be the electron scanning microscope incorporated into the specimen chamber. This microscope, which will use a field emission electron source, will permit high resolution observation of the surface topology while sputtering analysis is taking place. In addition, it is hoped that it will be possible to use the high intensity scanning electron beam to generate ions for the mass spectrometer. This could occur either through impact ionization desorption, or through any beam-sputtered material interaction which changes the ion sputtering yield.

Other analysis techniques which might be built into the instrument could include Auger electron analysis, proton scattering, LEED, or field ion microscopy.

2.0 Electron Ionization Cross Sections

Personnel: C.K. Crawford; K.L. Wang

Sponsorship: Air Force Materials Laboratory

The electron-impact ionization cross-section program using a large quadrupole mass spectrometer is continuing. New measurements have been made

on the ionization cross-sections for monatomic and polyatomic carbon. Previously reported difficulties in obtaining stable carbon beams of reasonable intensity have now been largely overcome. The measurements will be published soon.

The equipment improvement campaign necessary to prepare for these measurements is continuing. Beam stabilizing feedback controllers have been added, as has been a new higher gain electron multiplier assembly. A continuing problem is that power limitations for the bombardment-heated Knudsen cell, presently result in a restriction on carbon source size. This restriction results in low source charges and undesirably short operating times. A larger power supply is being obtained.

As an additional means of calibrating neutral beam intensity, a quartz-crystal thin-film thickness monitor was installed to be interchangeable with the normal atomic beam (weight-gain) trap. The quartz gauge provides a direct readout of the mass gain due to condensed vapor in real time.

Another new cross section measuring technique, the exponential depletion method, has been developed in theory. The method is similar to the multiple cross beam technique previously described, in that a neutral beam is directed through intersections with two separate electron beams. The exponential depletion method, however, can determine absolute cross sections without ever measuring the actual value of any ion current. This is advantageous since mass spectrometers with unity ion transmission appear to be unachievable. The technique is similar to that sometimes used to measure optical absorption.

3.0 Ion Sources for Implantation and Surface Reactions

Personnel: F.G. Ruedenauer; C.K. Crawford

Sponsorship: NASA Electronics Research Center, Lincoln Laboratory

A project designing ion sources for use both in ion implantation and in the study of bombardment-induced surface chemical reactions has been completed. Both gas and metal vapor sources were constructed to provide microampere currents at high brightness, good charge efficiency, and low power consumption. The sources are of the Unoplasmatron type, and are very small in size (one inch in diameter including all heat shielding). Using ions such as Argon, Lead, and Gallium, brightnesses of better than $0.1 A/cm^2 sr$ at 2kv were reliably obtained. Total input power for Gallium (operating at a temperature of 1400°K) is a little over 100 watts.

Several experiments were undertaken to study the effect of ions in

exposing photoresists. These experiments are continuing.

4.0 Electron Ion Beam Testing of Microcircuitry

Personnel: C.K. Crawford; P.E. Kudirka

Sponsorship: Unfunded

It has been determined that small electron beams, about one micron in diameter, could be used to test electronic microcircuits. The beams would be focused either onto small contact pads built onto the circuits, or directly onto the thin film wiring. A study of available electron sources and lens-aberration constants shows that currents of about one microampere could be obtained in a one micron beam with a ten kilovolt beam energy. The beams would cause negligible heating in a target which had the thermal conductivity of silicon, and excessive electron penetration should not be a problem. Space charge would be negligible.

The problem of reading voltages out of a microcircuit, necessary both for injecting voltage signals into a circuit (as distinguished from current signals) and for obtaining signal readout, could be solved in at least two ways. The secondary electron spectra resulting from the microbeam bombardment could be used to measure surface potentials with an accuracy of considerably better than one volt; work to design such a detector is in progress. Or, an electron mirror microscope could be used to measure potentials; this method, however, appears much more complex. A third possibility would be to use a thin film electron emitter built into the circuit; at present this technique seems totally impractical.

To test a real microcircuit requires measurement of many potentials and injection of many signals simultaneously, The best method appears to be to use a matrix electron gun delivering many separately controlled electron beams, along with one secondary electron detector. Secondary electrons due to the various beams would be identified by a low-amplitude high-frequency characteristic modulation on each beam, which would be ignored by the digital microcircuit under test.

Thesis:

A. Shigamoto, "A Study of the Electron Microscope", S.B. Thesis, Department of Electrical Engineering, June 1969.

L.L. Wischhoefer, "Secondary Electron Emission Characteristics of Stainless Steel in Graphite," S.B. Thesis, Department of Electrical Engineering, June, 1969.

Publications:

C.K. Crawford, "Electron Ionization Cross Sections for Hard to Vaporize Materials," invited paper, 17th Annual Conference on Mass Spectrometry and Allied Topics, May 18-23, 1969, Dallas, Texas, page 15.

K.L. Wang, M.D. Brody, C.K. Crawford, "Electron Impact Ionization Cross Sections, Particle Optics Laboratory TR-3" (56 pages, 18 figures) January 1969.

F.G. Ruedenauer, "A Mass Analyzer System for the High Voltage Terminal of a van de Graff Heavy Ion Accelerator," IEEE Trans. Nucl. Sci. NS-16, 3 (1969) 35.

C.K. Crawford, "Standards Under the Belljar," Industrial Research, 11 (Sept. 1969) 64.

METALLURGY AND MATERIALS SCIENCE

I. PHYSICS OF SOLIDS

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

B. L. Averbach, Professor
Roy Kaplow, Associate Professor
S. C. Moss, Associate Professor
D. J. Sellmyer, Assistant Professor
K. H. Johnson, Assistant Professor

Research Staff:

J. W. Brackett, Research Associate
J. F. Graczyk, Research Associate
Sally Duren, DSR Staff, Center for Materials

Graduate Students:

H. R. Beumer, Research Assistant
G. R. Caskey, Research Assistant
W. K. Choo, Research Assistant
R. Currat, Research Assistant
W. S. Ewing, NSF Trainee
J. W. Franz, NSF Trainee
I. S. Goldstein, Research Assistant
S. C. Lee, Research Assistant
K. R. Morash, Research Assistant
M. D. Rechtin, Research Assistant
A. L. Renninger, NSF Trainee
R. Shemenski, NSF Trainee
D. J. Silversmith, Research Assistant
J. A. Yasaitis, Teaching Assistant
J. Zagarins, Research Assistant

Support Staff:

G. Pishenin, Engineering Assistant
Frances M. Gedziun, Secretary
Anne W. Howe, Secretary

Personnel who have left:

G. R. Caskey, Research Assistant, Metallurgy (Now at E. I. du Pont de Nemours & Company)

I. S. Goldstein, Research Assistant, Metallurgy (Now at Xerox Research Laboratory)

R. Shemenski, NSF Trainee, Metallurgy (Now at Great Lakes Research)

D. J. Silversmith, Research Assistant, Metallurgy (Now at Bell Telephone Laboratories)

R. Currat, Research Assistant, Metallurgy (Army Materials Mechanics Research Center)

Degrees Granted:

G. R. Caskey, Ph.D., Metallurgy, January 1969

R. Currat, Ph.D., Metallurgy, July 1969

I. S. Goldstein, Ph.D., Metallurgy, August 1969

S. C. Lee, M.S., Metallurgy, July 1969

R. Shemenski, Ph.D, Metallurgy, January 1969

D. J. Silversmith, Ph.D., Metallurgy, June 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 71622; 71626; 75121; 75123; 75125; 78892

Air Force Office of Scientific Research, F44620-69-C-0054, DSR 71446

Atomic Energy Commission, AT(30-1)-1002, DSR 76831

John Simon Guggenheim Memorial Foundation

National Aeronautics and Space Administration, NAS 12-2040, DSR 71329

National Science Foundation, NSF GP-5463, DSR 76275; GK-1947, DSR 70847; GJ-129, DSR 71743; GK-2911, DSR 71029

Office of Naval Research, Nonr-1841(35), DSR 71362

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

United States Steel Corporation, DSR 70216

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

Xerox Corporation, DSR 74997

Research Report

Much of the research in the physics of solids group is concerned with the more complex forms of condensed matter. For example, electron transport properties are being studied in alloy systems and in intermetallic compounds as opposed to the simple pure materials. The structure and physical properties of liquids, amorphous materials, and alloys are being investigated in contrast to similar work on high purity single crystals. 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; magnetism in alloys; band calculations in alloys and compounds; and photoconductivity in amorphous materials. Research programs in these areas are described in the following sections.

1.0 Spin Correlations in Magnetic Materials

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

Sponsorship: National Science Foundation

The arrangement of spins in ferromagnetic and anti-ferromagnetic materials is being investigated by means of magnetic neutron scattering measurements. Single crystals of the anti-ferromagnetic series MnO, NiO, and CoO, are being measured at temperatures just above and below the Neel temperature. Correlations have been observed above the critical at distances well beyond the 20th nearest neighbor, and the development of long range anti-ferromagnetic order has been followed as the temperature is lowered through the critical. Twin and spin domains have also been observed in these materials, and it has been shown that the domain population is greatly affected by the application of pressure. These data are being used to evaluate magnetic interaction energies and to provide a basis for theories of magnetic critical phenomena.

2.0 Elastic Constant Studies of Beryllium

Personnel: B. L. Averbach; D. J. Silversmith
Sponsorship: Wright Air Development Center

The elastic constants of beryllium and of alloys containing 1.1 and 2.4 wt pct copper (0.16 and 0.35 at pct) have been measured by a pulse-echo-overlap method. These stiffness coefficients in units of 10^{12} dynes/cm^2 are

crystal	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}
Be	2.932	3.561	1.706	0.236	0.00
Be-1.1 Cu	2.948	3.597	1.702	0.278	-
Be-2.4 Cu	2.931	3.552	1.731	0.301	0.03

The effect of hydrostatic pressures up to 6 kilobar is indicated by the pressure derivatives given below:

crystal	$\frac{dC_{11}}{dP}$	$\frac{dC_{33}}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{dC_{12}}{dP}$	$\frac{dC_{13}}{dP}$
Be	6.87	8.98	2.55	2.72	3.3
Be-1.1 Cu	7.13	7.79	2.62	2.86	-
Be-2.4 Cu	12.01	13.42	2.58	7.73	-2.8

The coefficient $C_{13} = 0$ is unusual for a metal; this value indicates that there is no coupling between a tensile stress along the c-axis and a resolved stress in the basal plane. This anisotropy in the bonding mechanisms for the two principal directions has been correlated with the band structure and may account for the relatively easy cleavage of beryllium along the basal plane.

These studies, along with the associated work on Compton scattering, Fermi surfaces, and band calculations reported in sections which follow, are being used to reconsider the bonding mechanisms in beryllium. Unusual anisotropies have been observed in each of these measurements, and it appears that there may be considerable covalent character to the bonding along the c-axis.

3.0 Atomic Arrangements in Selenium

Personnel: Roy Kaplow, B. L. Averbach; Alan Renninger
Sponsorship: Xerox Corporation

A study is being made of the structure of vitreous and crystalline selenium and of selenium-arsenic alloys. X-ray diffraction data are being used to obtain radial distribution functions, and the radial distribution functions are then interpreted by means of computer models. The computer method uses a Monte Carlo procedure to move atoms from an initial array until a satisfactory fit is obtained to the radial distribution function. This approach is being used in amorphous alloys in the vicinity of As_2Ge_3 and As_4Se_4. The amorphous structures are being compared with the corresponding crystalline material.

4.0 Photoconductivity Measurements in Amorphous Materials

Personnel: B. L. Averbach; Mitchell Kuninsky
Sponsorship: Advanced Research Projects Agency

Measurements are being made of the photoconductivity in selenium and selenium-arsenic thin films. Nanosecond light pulses are being used in order to avoid space-charge defects. The mobility of the electron and holes is being investigated as a function of temperature and alloy composition.

5.0 The Structure of Liquids

Personnel: Roy Kaplow, B. L. Averbach; Sang C. Lee
Sponsorship: National Science Foundation

Atomic pair distributions are being measured in solutions of HCl in H_2O, with the primary intention of obtaining information regarding the role played by the excess protons in intermolecular O-O bonding. Results obtained so far indicate that an extreme perturbation of the water structure is caused by the HCl, including the establishment of shorter correlation distances.

6.0 Compton Scattering

Personnel: Roy Kaplow; Roland Currat
Sponsorship: Wright Air Development Center

A high resolution, Soller slit geometry, automated X-ray spectrometer was used to measure the Compton line profiles of oriented beryllium single crystals. These energy distributions of inelastically scattered photons were analyzed in terms of the electron momentum distribution in the beryllium.

Anisotropies exist in the low electron momenta region, and are attributed to the conduction electrons. An enhancement of the charge and momentum distributions in the basal plane is indicated and geometrically consistent with the anomalous c/a ratio. Within the basal plane enhancement is indicated along near-neighbor directions. The experimental "Fermi momentum" is also angularly dependent.

Application of an atomic scattering model, proposed by Bloch, to the available Hartree-Fock calculations for the core electron distribution accounts for the experimental assymetry in the high momentum tails of the profile. However, the total profiles cannot be accounted for in detail in terms of existing calculations.

7.0 Mössbauer Effect in Iron Alloys

Personnel: Roy Kaplow; W. K. Choo (in cooperation with Professor Morris Cohen)
Sponsorship: Office of Naval Research

This research concerns the measurement of Mössbauer spectra in alloys of iron with interstitial type elements, particularly carbon, and with some substitutional atoms. Specimens are being produced by splat-quenching, which allows the formation of unusual phases. Also of interest is the inhibition of diffusion controlled rearrangements which may occur, in ordinary quenching, during the formation and cooling of well known phases.

8.0 On-Line Systems for Numerical Analysis

Personnel: Roy Kaplow; J. Brackett; Terence Colligan
Sponsorship: Project MAC, and Advanced Research Projects Agency

Virtually all on-line systems for numerical analysis allow the user to form secondary level operators in terms of a group of built-in primary operations. Such secondaries are expedient, but also tend to be inefficient compared to a compiled primary of identical purpose. On the other hand, the user, who might otherwise write a primary operator, is rarely prepared to implement those individual analyzing programs which trap and comment on errors in usage, and which ordinarily accompany the built-in primaries in a useful system.

It is desireable therefore, both for the casual user and for the initial building-up of a system, that these functions be centralized within the system, essentially as part of the input-language processor. One also requires a simple mechanism for specification of error tables for each new primary; preferably, this would be part of an interactive add-an-operator operator.

Such a processor has been designed and partially implemented.

9.0 The Structure of SiO

Personnel: Roy Kaplow; John Yasaitis
Sponsorship: Advanced Research Projects Agency

X-ray diffraction techniques, which have been applied previously to the measurement of structures of amorphous selenium and B_2O_3, are being used to investigate the structure of SiO. Samples of the material have been supplied by the Los Alamos Research Laboratory.

10.0 Teacher-Interactive Computer System

Personnel: Roy Kaplow; John Linderman
Sponsorship: National Science Foundation

An on-line computer sub-system has been designed, and is being implemented, with the purpose of providing an effective mechanism for teachers to develop computerized tutorial programs.

11.0 Alloy Photo-Emission and Surface Effects

Personnel: Roy Kaplow; William Ewing
Sponsorship: Advanced Research Projects Agency

Appropriate high-vacuum apparatus has been designed and is being assembled (with spectroscopy equipment), for the purpose of measuring the intensity and energy distribution of electrons emitted in response to ultra-violet excitation. Alloy surfaces will be examined in various controlled conditions in order to study the distribution of electron states in the alloys, the process of photon absorption and electron transition, and the nature and effects of surface contaminants.

12.0 Quantum Oscillatory Phenomena in Dilute Beryllium-Copper Alloys

Personnel: D. J. Sellmyer, B. L. Averbach; I. S. Goldstein
Sponsorship: Advanced Research Projects Agency and Wright Air Development Center

The de Haas-van Alphen effect has been investigated in pure beryllium and in Be-Cu alloys containing up to 0.34 at. pct. Cu. The extremal cross-sectional areas of the cigar-shaped second double-zone electron pieces were observed to decrease with alloying. On the other hand, the areas of the coronet-shaped first double-zone hole piece increased with alloying. In the more dilute alloys this can be satisfactorily explained by the rigid band theory. However, for the highest concentration alloy, all of the extremal cross-sections showed a significant deviation from rigid band behavior. A large part of this deviation is caused by the increase in c/a ratio with alloying. The remaining relative deviation was found to be correctly predicted by a non-rigid band model using an effective screening length.

An amplitude analysis of the de Haas-van Alphen results showed that there is a significant anisotropy in the scattering temperature as a function of alloying. This implies that electrons travelling parallel to the basal plane are scattered more strongly by the copper atoms than those travelling perpendicular to the basal plane. Within experimental error, the cyclotron mass was found to be independent of alloying.

Magnetic breakdown has been investigated in pure beryllium in fields up to 150 kG. High-field magnetoresistance measurements of open orbits in the basal plane showed that at 150 kG, the height along [0001] of the breakdown region of the cigar is approximately 12% (0.10 a.u.) of the length of the cigar. It was possible to fit the field dependence of the Shubnikov-de Haas effect with a correction factor for breakdown which included a characteristic breakdown field (B_o) of 100 kG, although the fit is not very sensitive to the exact value of B_o.

13.0 Fermi Surfaces in Alloys

Personnel: D. J. Sellmyer (in cooperation with Dr. J. Ahn, IBM)

Sponsorship: Advanced Research Projects Agency

Fermi surface experiments such as the de Haas-van Alphen effect, high-field magnetoresistance, and Hall effect are being performed in several highly ordered metallic compounds and also in dilute solid solutions. The object of the work is to study the quantum chemistry of the ordered alloys through their band structures and to investigate the influence of alloying on the E(k) relation in the dilute alloys. The experiments are performed in fields up to 150 kOe at the Francis Bitter National Magnet Laboratory or in our own 100 kOe superconducting solenoid. Recent results, as yet unpublished, have been obtained on the compound $AuSb_2$, and on dilute PbIn alloys. Further studies on new alloy systems, with emphasis on transition-metal alloys, are planned.

14.0 Transport Properties of a Memory-Type Chalcogenide Glass

Personnel: D. J. Sellmyer (in cooperation with Professors

D. Adler and S. D. Senturia); J. M. Franz
Sponsorship: Advanced Research Projects Agency

Transport measurements have been performed on the conducting state of a memory-type chalcogenide glass, of composition $Te_{81}Ge_{15}As_4$. D.C. resistivity measurements below $300^{\circ}K$ indicate no carrier freeze-out down to $4.2^{\circ}K$. $\rho(300^{\circ}K)/\rho(4.2^{\circ}K)$ was found to be 2.5. A.C. conductivity measurements at $300^{\circ}K$ showed only an 18% increase in $\sigma(\omega)$ up to 150 kHz. Hall effect experiments at 100 Hz showed no dependence of carrier concentration on temperature between 77 and $300^{\circ}K$, and indicate a room temperature mobility of 85 $cm^2/V\cdot sec$. The charge carriers are holes. The magnetoresistance, measured at $1.6^{\circ}K$ up to 140 kOe, was positive with saturation beginning to set in above about 80 kOe. The results of these studies, taken in conjunction with X-ray and NMR data, suggest that the conducting state of these glasses is obtained from a spinodal decomposition or phase separation above $230^{\circ}C$ into alternating regions of primarily crystalline GeTe and primarily crystalline As-doped Te. These regions are both degenerate p-type material.

15.0 Electron Scattering from Localized Moments in Metals

Personnel: D. J. Sellmyer; J. Zagarins
Sponsorship: National Aeronautics and Space Administration-Electronics Research Center

An experimental investigation of the thermoelectric power and resistivity of dilute magnetic alloys is in progress. A Kondo effect has been observed in a dilute Ag(Fe) alloy with $T_k \simeq 10^{\circ}K$. We intend to study the behavior of the spin-compensated state as the properties of the host matrix are varied. This will be done by changing the density of states at the Fermi level, N(O), through alloying Ag with Pd. While the theory of the s-d interaction is not well understood in transition metal hosts, one might expect T_k to vary dramatically upon changing N(O) by alloying. Thus, since N(O) is known in the alloys it should be possible to obtain information on the effective exchange parameter as well as spin-compensation in two-band hosts.

16.0 Localized Moments in Intermetallic Compounds

Personnel: D. J. Sellmyer; G. R. Caskey, J. M. Franz
Sponsorship: Advanced Research Projects Agency

The nature of the magnetic impurity states is being investigated in the transition metal-aluminum intermetallics M Al where M = Fe, Co, or Ni. These compounds have the CsCl structure at exact stoichiometry and the impurity states are associated with excess M atoms on Al sites in the lattice. Local moment formation in this series of alloys is interesting because the Fermi surface is expected to drop from a position just above - to a position within - the d bands on going through the series NiAl, CoAl, FeAl. Electrical resistivity, thermopower, and magnetoresistance measurements have already been performed between 1.2 and 300°K. Local moments exist in all the alloys but a Kondo effect appeared only in the CoAl case. At present, low temperature susceptibility measurements are being made to obtain a consistent picture of the s-d interaction and spin-compensation in these alloys.

17.0 Diffuse Scattering and Fermiology in Alloys

Personnel: S. C. Moss
Sponsorship: John Simon Guggenheim Memorial Foundation

We have shown how the Fermi surface of a disordered alloy will be reflected in the local-order diffuse scattering of X-rays, etc., through anomalies similar to those predicted by Kohn for phonon scattering. These ideas have been applied to the existing data on the splitting of the diffuse spots from Cu-Au alloys above T_c and, more tentatively, to the <111> scattering profile from βCuZn. The results indicate that disordered Cu_3Au has a Fermi surface very much like copper's while disordered $CuAu_3$ resembles gold. The copper-gold alloys provide an extremely sensitive test because both Cu and Au are one-electron metals and their Fermi surfaces differ by only a few percent in the critical dimensions.

18.0 Short Range Order in Copper-Aluminum Alloys

Personnel: S. C. Moss (in cooperation with Professor M. Bever and Dr. R. O. Scattergood)
Sponsorship: Atomic Energy Commission

The diffuse scattering of X-rays has been measured in three single crystal alloys containing 6, 11 and 16 at. pct. aluminum. Our results reveal a pronounced diffuse satellite intensity in the 11 and 16 pct. crystals which appear in a four-fold symmetrical fashion about the usual f.c.c. superlattice positions. From the composition dependence of the satellite peak positions - using both our results and those of other workers - we were able to show that these peaks have their origin in the Kohn-type anomalies invoked earlier by S. C. Moss in explanation of similar results in copper-gold alloys. The shifting of the peaks with composition provides a very sensitive determination of the variation in k_F <110> (the value of the Fermi wave vector in the <110> direction) with alloying. Our interpretation is borne out both by a simple free-electron scaling of the copper Fermi surface and by a recent positron annihilation study of the Cu-Al alloys.

19.0 The Structure of Amorphous Silicon

Personnel: S. C. Moss; J. F. Graczyk
Sponsorship: Advanced Research Projects Agency

The atomic arrangements and mode of crystallization in vapor-deposited films of amorphous silicon have been investigated using elastic electron diffraction. We have studied the thickness and temperature dependence of the diffuse diffraction pattern and have taken selected Fourier transforms of our intensity profiles in order to determine the radial density function (RDF). In addition we have investigated microcrystallite models and have performed selected low angle electron scattering experiments. The results can be briefly summarized.

1. Amorphous Si has a very well-defined tetrahedral cluster of nearest neighbors at exactly the crystalline nearest neighbor distance of 2.35 Å.

2. The second neighbor peak in the RDF while it occurs

at nearly the crystalline distance, is much broader than the first and is rather asymmetric. This tells us about the variation in tetrahedral bond angles and about the disposition of tetrahedra with respect to each other.

3. The density is close to the crystalline density if one excludes the grown-in voids or pores. If these are included, as they invariably are in bulk density measurements, the density defficiency can exceed 15%.

4. Multiple scattering of electrons has the effect not only of adding a background intensity but of appreciably damping out the oscillations in the intensity patterns from thicker films.

5. As the films are heated up, the pores or voids begin to anneal out - as seen in the low angle scattering - and finally the amorphous Si crystallizes in an obviously heterogeneous way. As crystallization proceeds the first diffuse peak shifts up to and becomes the (111) diamond cubic peak and the (220)-(311) pair grows out of the second peak.

6. Amorphous Si, as confirmed by a variety of tests, is not just a finely dispersed aggregate of microcrystals of the diamond cubic structure.

20.0 Temperature Dependence of Electron Diffraction Intensities

Personnel: J. F. Graczyk
Sponsorship: Advanced Research Projects Agency

Using our scanning diffraction instrument, the elastic diffraction pattern from polycrystalline aluminum foils was measured at 300°K and 77°K over a range of thicknesses from 700 Å to 2500 Å. The results verified the strongly dynamic nature of the scattering and demonstrated the logarthymic thickness dependence of intensity ratios at the two temperatures. Essentially the study showed how dynamic diffraction produces a temperature dependent absorption coefficient for electrons. The results yielded excellent agreement with predictions based on the two-beam approximation of Boersch, Jeschke and Raith but only in a range of thickness where the theory is presumably invalid. The experiments thus await a better theory.

21.0 Ultrasonic Studies of Interstitial Phases

Personnel: S. C. Moss (in cooperation with Professor R. M. Rose and Dr. K. A. Jones)
Sponsorship: U. S. Steel Corporation and the National Science Foundation

Ultrasonic velocity and attenuation data were collected on a Nb single crystal with and without a small amount of dissolved interstitial oxygen. The measurements were made as a function of temperature from $4^{o}K$ to $300^{o}K$ and revealed no order-disorder reaction in the oxygenated crystal. The $4^{o}K$ attenuation (below the superconducting T_c) showed predictable behavior for the clean crystal but the effect of dissolved oxygen was to introduce oscillations into this attenuation. This result could be simply interpreted in terms of clustering of the oxygen interstitials which interpretation was corroborated by a variety of other data.

22.0 Theoretical Electronic Structure of Polyatomic and Macro-Molecules

Personnel: K. H. Johnson; F. C. Smith, Jr.
Sponsorship: Air Force Office of Scientific Research

A new approach, based on scattering theory and Green's function formalism, has been developed for calculating from first quantum-mechanical principles the electronic structures of polyatomic and macro-molecules. The computational simplicity of the method and its applicability to molecules of arbitrary stereochemical structure are of particular advantage in treating systems where more conventional molecular-orbital techniques are difficult to implement. Among the most novel features of the method are: (1) the adoption of a model single-particle Hamiltonian based on the use of local, statistical approximations to exchange and correlation; (2) the complete freedom from having to calculate multicenter integrals (such as those of conventional LCAO techniques); (3) the explicit separation of numerical quantities into those which depend only on the nature of the component atoms or ions in

the molecule and those which depend exclusively on the molecular geometry. Initial non-self-consistent calculations have been completed on several elementary diatomic molecules, including H_2^+, H_2, C_2, and LiH, for the purposes of testing computer programmes and calibrating the model. More recently, these calculations have been extended to include self-consistency within the framework of the model Hartree-Fock Hamiltonian. General, self-consistent programmes are now being coded for the treatment of polyatomic systems, and applications are being made to complex sulfur and chlorine oxy-anions. Future applications will include transition-metal complexes, in particular, those important to biology, such as the metal porphyrines. Applications to macro-molecular systems, including polymers, biopolymers, and amorphous solids, are also planned.

23.0 Theoretical Electronic Band Structures and Fermi Surfaces of Metals and Alloys

Personnel: K. H. Johnson
Sponsorship: Advanced Research Projects Agency

Recently, our primary efforts have been directed to the calculation, from first quantum-mechanical principles, of the electronic band structures and Fermi surfaces of ordered alloys. Calculations by the Korringa-Kohn-Rostoker (KKR) method have been completed for the intermetallic compounds β'AuZn and β'NiAl, both of which are Hume-Rothery "3/2" type alloys having the cesium chloride crystal structure. The energy bands and Fermi surface of β'NiAl are quite similar qualitatively to those determined earlier for ordered beta brass (β'CuZn), with overlap of the Fermi surface with the second (dodecahedral) zone boundary contributing in an important way to the stability of the NiAl beta phase. On the other hand, in β'AuZn relativistic contributions to the electronic structure lead to "spin-orbit" splittings of the bands and to other band distortions which, in turn, cause a relatively large discontinuity of the Fermi surface across the first (cubic) zone boundary. This discontinuity tends to stabilize the ordered phase, and is consistent with the fact that β'AuZn does not disorder appreciably below the melting temperature. The very striking optical properties of the alloys

studied, e.g., the pale pink color of β'AuZn at room temperature and the composition dependence of the reflectance of β'NiAl, have been explained in terms of electronic transitions occurring between occupied and unoccupied bands in the vicinity of the Fermi energy.

24.0 Theoretical Electronic Structure and Cohesive Properties of Beryllium

Personnel: K. H. Johnson; D. O. Pettijohn, D. Klingspon (Physics Dept.), (in cooperation with Professor P. D. Decicco, Physics Dept.)

Sponsorship: Advanced Research Projects Agency

In view of the technological importance of beryllium, it is perhaps surprising that there has been little theoretical research into the relationship of the electronic structure of the metal to its material and mechanical properties. Recently in our laboratory, there has been a concentrated effort to apply basic experimental methods of solid-state physics to beryllium. This work has included measurements of the elastic constants, the determination of electron momenta via Compton scattering, and Fermi surface measurements as a function of alloying small amounts of impurities. Electronic structure calculations are being carried out from first principles by the Korringa-Kohn-Rostoker (KKR) method on the IBM 360-Model 65 computer, using the constant-energy-search programmes developed in previous work. This procedure leads to a direct mapping of theoretical Fermi surface cross sections, as well as to the generation of energy band profiles. We are devoting particular attention to the dependence of the electronic structure on: (1) the choice of statistical exchange potential; (2) the c/a ratio of the hexagonal close-packed (hcp) lattice; (3) non-spherical components of the crystal potential. Energy band calculations on beryllium oxide (BeO), which has unusual high-temperature properties, are also planned. We have also extended the scope of our work well beyond the calculation of energy bands by attempting to develop a quantitative theory of the elastic properties of beryllium. A procedure which has proven to be practicable, in principle, involves the following

considerations. The atomic force constants, which determine the elastic and vibrational behavior of crystals, are the components of the change in force produced on the nuclei when in equilibrium positions by the infinitesimal displacements of a single nucleus. Such quantum-mechanical forces can be calculated directly from the electronic and nuclear charge distributions by Coulomb's law and Feynman's theorem. Localized perturbation theory can then be used to calculate, to first order, the change in conduction electron density (and hence the force constants) resulting from the infinitesimal nuclear displacement. The elastic constants can then be related to sums of the atomic force constants for comparison with measured elastic properties. Such calculations are now being initiated on beryllium, as well as on simpler hexagonal metals such as magnesium. Finally, an attempt is presently being made to develop a quantitative theory of the Compton data recently measured for beryllium. Problems of fundamental importance in this connection include: the validity of the traditional "impulse approximation" and the nature of the initial and final electronic states of the Compton process. In summary, by investigating the theoretical electronic structure of beryllium and its dynamical behavior at the atomic level, we hope to be able to understand, at least in part, the measured macroscopic electronic and cohesive properties.

25.0 Theory of Impurity and Surface Electronic States

Personnel: K. H. Johnson
Sponsorship: Advanced Research Projects Agency

A multiple-scattering model, based on Green's function formalism, has been developed for the theoretical determination of the localized electronic states of impurities in crystals. This model has the advantage over other methods that it does not require an explicit knowledge of the Wannier or Bloch wave-function spectrum for the perfect crystal. Because the impurities and atoms of the host lattice are treated on an equal basis, one can set up the model for the treatment of multiple impurities forming clusters, lines, and planes in the crystal, as easily as for the isolated impurity. The technique is

applicable, in principle, to all classes of crystals and impurities, including transition and magnetic elements, where a "muffin-tin" representation of the impurity potentials is a reasonable first approximation. Vacancies are also within the scope of the model. More recently the model has been extended to the problem of calculating surface electronic states.

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R. Currat, "X-Ray Investigation of the Electronic Momentum Distribution in Beryllium Single Crystals", Ph.D., Department of Metallurgy and Materials Science, July 1969.

I. S. Goldstein, "Fermi Surface of Beryllium and Beryllium-Copper Alloys", Ph.D., Department of Metallurgy and Materials Science, August 1969.

S. C. Lee, "Studies on the Structure of HCl Solutions", M.S., Department of Metallurgy and Materials Science, July 1969.

R. Shemenski, "Neutron Magnetic Scattering from a NiO Single Crystal", Ph.D., Department of Metallurgy and Materials Science, January 1969.

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

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

M. Cohen, Ford Professor of Materials Science and Engineering
J. F. Breedis, Associate Professor

Research Staff:

M. K. Koul, Research Associate
A. J. Gregor, Technical Instructor

Graduate Students:

J. W. Pugh, Part-time Instructor
A. M. Sherman, Part-time Instructor
G. T. Eldis, NASA Trainee
F. B. Fletcher, NSF Fellow
D. S. Gelles, NSF Trainee
M. K. Korenko, NDEA Fellow
R. K. Mehrotra, Research Assistant
D. B. Snow, Research Assistant
R. Stevenson, Research Assistant

Support Staff:

Miriam E. Yoffa, Engineering Assistant
Robert Goss, Technician
Jane K. Operacz, Technician
Kathleen L. Fletcher, Secretary
Marguerite A. Meyer, Secretary

Personnel who have left:

Dr. M. K. Koul, Research Associate (Now at Union Carbide Corporation, Niagara Falls, New York)

Degrees Granted:

None

Sponsorship:

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Air Force Materials Laboratory, Contract F33615-69-C-1603, DSR 71596
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Climax Molybdenum Company, 21836
Office of Naval Research, Contract No. N00014-67-A-0204-0027, DSR 71362
NDEA Fellowship
NSF Fellowship
NASA Traineeship

Research Report

1.0 Strain-Enhanced Diffusion

Personnel: M. Cohen

Sponsorship: None

Plans are underway to determine the effect of concommitant plastic deformation on the diffusion of interstitial carbon in body-centered cubic and face-centered cubic iron. The strain enhancement of self-diffusion and substitutional diffusion is now well established, the proposed mechanism being that of "pipe" migration along moving dislocations. An equivalent process for interstitial diffusion has been postulated.

2.0 Nucleation of Martensitic Transformations

Personnel: M. Cohen; M. K. Korenko

Sponsorship: Office of Naval Research

Further measurements are being carried out on the nucleation rates of iron-nickel and iron-nickel-manganese martensites, using quantitative metallography and kinetic calculations. Models have been developed to take autocatalytic and partitioning effects into account. To establish the nature of the preferred nucleation sites, the transformation is being followed in very small particles which can be completely viewed at one time within the field of an electron microscope. A cooperative program has been instituted with the Research Center of the United States Steel Corporation, making use of their million-volt electron microscope.

3.0 Mössbauer Investigations of Iron-Base Interstitial Phases

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

Sponsorship: Office of Naval Research

Considerable time was devoted to improving the operation and reliability of the Mössbauer equipment. Runs are now in progress with very high-carbon iron-carbon martensites which are austenitic at room temperature, and which can be converted to virgin martensite by refrigeration. The specimens have to be splat-quenched from the liquid state for this purpose, in order to avoid inadvertent precipitation of carbides at elevated temperatures. We are now in a position to determine the local environments of the interstitial atoms in virgin body-centered tetragonal martensite; in addition, the subsequent changes due to re-distribution of the carbon atoms on warming up from the liquid-nitrogen temperature will be followed to obtain evidence of carbon-clustering, carbon disordering (conversion from tetragonal to cubic martensite), carbon migration to dislocations, and carbide precipitation.

Splat-quenched specimens have also been prepared of the new epsilon-phase, which appears to be an ordered solid-solution of carbon in the hexagonal close-packed form of iron, based on a unit-cell composition of $Fe_{12}C_3$. This phase will be studied by Mössbauer measurements. Here again, the nature of the carbon-atom environments is of special interest.

4.0 Strain Hardening at Very Large Plastic Deformations

Personnel: M. Cohen, J. F. Breedis; A. M. Sherman

Sponsorship: Office of Naval Research

The strain hardening of iron-base and titanium-base alloys during very severe plastic deformation by wire drawing are being investigated from the standpoint of the mechanisms involved. For the ferrous materials, the main strengthening process is one of cell formation within the grains, and the progressive refinement of these cells. A quantitative model has been developed, and is being tested for the titanium alloys. A significant part of the cellular-refinement process is controlled by dynamic recovery during the deformation, which results in cell-wall migration and some loss of cells. The nature of this recovery phenomenon is being examined, particularly with reference to its temperature dependence.

5.0 Strengthening Mechanisms

Personnel: M. Cohen; G. T. Eldis, F. B. Fletcher

Sponsorship: Office of Naval Research; Bethlehem Steel Corporation

The thermomechanical strengthening of iron-base alloys is being

investigated in a series of alloys designed to distinguish between the role of carbon/dislocation interactions and actual carbide precipitation. Both ausforming and strain tempering are being analyzed in this way. All of the transformation temperatures are below the ambient in order to start with virgin martensite.

A relatively new phenomenon, the so-called strength differential, is under study in order to determine its cause and characteristics. For example, hardened steels are found to resist plastic deformation more effectively under uniaxial compression than under uniaxial tension, the difference being large enough to have considerable practical significance. The theoretical treatment of this strength-differential effect is still in an elementary stage, and the generality of the phenomenon remains to be ascertained.

5.0 Order-Disorder Phenomena in Iron-Carbon Martensites

Personnel: M. Cohen; A. M. Sherman

Sponsorship: Climax Molybdenum Corporation of Michigan

The relationship between tetragonal and cubic martensites is being studied with reference to the distribution of carbon atoms. A key issue in the current picture is whether the cubic form of martensite represents a disordered array of the interstitial carbon atoms, thus eliminating the tetragonal structure corresponding to the ordered configuration, or whether the martensite simply becomes depleted by virtue of carbon movement to dislocations and other structural traps. Experiments have been devised with iron-nickel-carbon alloys to distinguish between these alternatives, and to check the prevailing order-disorder theories.

6.0 Massive Transformations in Alloys

Personnel: M. Cohen; R. K. Mehrotra

Sponsorship: Office of Naval Research

The model of massive transformations proposed by D. A. Karlyn, J. W. Cahn and Morris Cohen earlier in this research program involves a delay time prior to the isothermal transformation, at least in the case of copper-zinc alloys. However, here the delay time is of the order of milliseconds, and is difficult to measure accurately. On the other hand, silver-cadmium alloys exhibit a massive transformation in which the reaction rates are very much slower. This provides an excellent opportunity to disclose the characteristics of the delay time, thereby providing a more rigorous test for the model.

7.0 Beta Isomorphous Titanium Alloys

Personnel: J. F. Breedis; M. K. Koul

Sponsorship: Air Force Materials Laboratory

The mechanical properties of beta isomorphous titanium alloys and their related transformation structures are of technological importance. Therefore, formation of the omega and alpha phases on quenching and aging and of martensite under an applied stress has been studied in binary alloys containing molybdenum, niobium and vanadium. Thermodynamic calculations using the regular solution approximation reveal that the beta phase exhibits a tendency for phase separation. Such compositional fluctuations in the beta phase can lead to an increase in the driving force for alpha phase formation in titanium-vanadium but are not associated with omega formation. Stress-induced martensite formed in molybdenum- and vanadium-containing alloys is found to be hexagonal close-packed, as expected from thermodynamic considerations. Furthermore, the influence of omega and alpha precipitation on the deformation behavior at normal strain rates has been studied. The apparent embrittling effect of omega is found to be associated with the large volume fraction and fine particle size of non-deformable precipitates. Prior omega formation is shown to influence the dispersion of alpha precipitates and to yield good tensile properties. Under high strain conditions, greatest strengthening is obtained after simultaneous deformation and transformation in metastable beta alloys and in alpha phase titanium where pressure-induced transformations are found to occur.

8.0 Strengthening Mechanisms in Titanium Alloys

Personnel: J. F. Breedis; D. S. Gelles

Sponsorship: Air Force Materials Laboratory; National Science Foundation Fellowship

A program to determine the effect of spinodal decomposition on the strength properties of beta titanium alloys is in progress. The titanium-niobium system which is believed to contain a hidden miscibility gap is the base system for this study. Employing Meijerings ternary regular solution model for miscibility gap formation and published heat of mixing data, the miscibility gap can be predicted to rise in temperature with additions of third components such as osmium, ruthenium, tungsten and zirconium to form a ternary monotectoid. Thusfar, the titanium-niobium-ruthenium and titanium-niobium-tungsten systems have been investigated. Phase separation has not been conclusively demonstrated as yet due to masking by an etching effect on electron microscopy specimens. However, the appearance of omega precipitation in high niobium-containing, Ti-Nb-W alloys after aging

suggests that phase separation may have occurred initially. The structures developed through aging will be studied using transmission electron microscopy, and low-angle x-ray scattering, and correlated with observed yielding and work hardening behavior.

A second portion of this effort is concerned with the influence of interstitial solutes and martensitic transformations on the mechanical properties of titanium alloys. Stable, beta titanium-molybdenum-oxygen alloys, as well as metastable compositions which transform to martensite on quenching are included in this new study.

9.0 Deformation of Hexagonal Close-Packed Alloys

Personnel: J. F. Breedis; D. B. Snow

Sponsorship: Advanced Research Projects Agency

The ultimate objective of this investigation is to elucidate the deformation behavior of single-phase hexagonal close-packed alloys over a wide range in composition. The ruthenium-iron system, where the hexagonal close-packed phase extends from zero to nearly eighty atomic percent iron, has been chosen for this study.

Single crystals of pure ruthenium have been obtained using the electron-beam floating-zone technique. Compression tests of these crystals indicate that only the $\langle 11\bar{2}0\rangle \{1\bar{1}00\}$ slip mode operates at room temperature. The critical resolved shear stress was determined to be 2.66 kg/mm^2. Deformation to the extent of 0.32 resolved shear strain reveals an unusually high rate of work hardening (8-19 kg/mm^2) during easy glide. Extensive studies of the dislocation configurations characteristic of stages I and II are being conducted. Foils made from sections spark cut parallel and perpendicular to the primary slip plane have been prepared. There is some tendency for clusters of edge dislocations to form, somewhat similar to those observed by Hirsch and Lally on the basal plane of magnesium single crystals. No evidence of dislocations with Burgers vectors other than $\frac{a}{3}\langle 11\bar{2}0\rangle$ has been detected by slip trace analysis or by dark field electron microscopy. The effect of temperature on the critical resolved shear stress and work-hardening rate of ruthenium crystals oriented for single slip, as well as for double slip and for compression parallel to the c axis are also being studied.

10.0 Fatigue of Titanium Alloys

Personnel: J. F. Breedis; R. Stevenson

Sponsorship: Advanced Research Projects Agency

The increasing use of titanium and its alloys in aerospace applications

has prompted extensive investigation of its macroscopic fatigue behavior. However, the microstructural response of titanium, or indeed of most H. C. P. metals to fatigue loading has been largely neglected. The purpose of this investigation is to observe the mechanical and microstructural response of titanium during the initial (hardening-softening) stage of fatigue. It is hoped that some correlation may be observed between the mechanical properties and the nature of the dislocation arrays which develop during this initial stage.

A conventional tensile machine has been modified to permit push-pull fatigue testing. No evidence of non-axiality can be detected in the range of plastic strain of interest. A separate control system has been developed which sets strain limits on the basis of plastic strain. In terms of sub-structural behavior, this strain limit is a more fundamental parameter than either stress or total strain. Incorporated into the system is the capability to suppress part of load scale which allows greater precision in determining when saturation has been attained. Since strain may also be displayed as either total or plastic strain, the mechanical response of the specimen during loading may be displayed in a manner which shows to best advantage the change in the property under consideration.

Preliminary results indicate that titanium (in common with some F. C. C. metals) develops a cellular dislocation structure as saturation is approached. Consideration is being given to the mechanisms by which this may occur.

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I. R. Sprung, J. F. Breedis, "Martensitic Transformation in Iron-Ruthenium," to be published.

III. PHYSICAL METALLURGY - Thermodynamics of Multicomponent Systems; Properties of Solid Solutions and Intermetallic Compounds; Deformation and Annealing.

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

M. B. Bever, Professor

Research Staff:

A. K. Jena, DSR Staff (to December 7, 1968)

G. C. Das, DSR Staff (from November 21, 1968)

Graduate Students:

J. P. Clark, NSF Trainee

J. W. Pugh, Teaching Assistant

Support Staff:

L. I. Sudenfield, Project Technician (to August 1, 1969)

T. R. Walsh, Secretary

Personnel who have left:

A. K. Jena, DSR Staff (Now Assistant Professor, Department of Metallurgical Engineering, Indian Institute of Technology, Kanpur, India)

Sponsorship:

Research carried out during the year under review was sponsored by the Office of Naval Research under Contract Nonr 3963-(19) as indicated; other research had no outside support. Several of the listed publications report research completed in earlier periods and supported by other agencies, in particular the U.S. Atomic Energy Commission under Contract AT(30-1)-1002.

Research Report

This research was concerned with the thermodynamics of multicomponent systems, the properties of solid solutions and intermetallic compounds and the deformation and annealing of metals and alloys. The experimental techniques used included liquid metal solution calorimetry, X-ray diffraction, electrical measurements and mechanical tests.

1. Thermodynamics of Multicomponent Systems

1.1 The Heats of Formation of Crystalline and Amorphous Selenium-Tellurium Alloys

Personnel: M. B. Bever; G. C. Das
Sponsorship: Office of Naval Research

The heats of formation at 273°K of crystalline selenium-tellurium solid solutions were measured by liquid metal solution calorimetry with bismuth as solvent. The entire composition range (10, 15, 20, 30, 50, 70 and 90 at. pct Te) was covered. All alloys had small negative heats of formation except the 20 pct Te alloy, which had a small positive heat of formation.

Amorphous selenium-tellurium alloys containing up to 40 at. pct Te were prepared by rapid solidification carried out by quenching capsules containing the molten alloy in a freezing mixture at -20°C. The heats of formation at 273°K, based on crystalline selenium and tellurium, of a 10 pct and a 20 pct Te alloy were positive and large. The measurements are being extended to amorphous alloys of higher tellurium concentration.

1.2 Energy of Ordering of the η-phase (Cu_6Sn_5) in the System Copper-Tin

Personnel: M. B. Bever; G. C. Das
Sponsorship: Office of Naval Research

The energy of ordering of the η-phase (Cu_6Sn_5) in the system copper-tin is being measured by liquid metal solution calorimetry. X-ray diffraction measurements of the state of order in specimens of this phase are in progress.

2. Properties of Solid Solutions and Intermetallic Compounds

2.1 Properties of Amorphous Selenium-Tellurium Alloys; Kinetics of Crystallization

Personnel: M. B. Bever; G. C. Das
Sponsorship: Office of Naval Research

The microhardness of amorphous alloys containing up to 40 at. pct Te

was measured. In this composition range the amorphous alloys showed a sharper increase in hardness with tellurium content than the crystalline alloys.

The microhardness of the initially amorphous alloys changed with time. At 45°C the hardness went through a maximum in a relatively short time; at room temperature it increased at a decreasing rate. The density of the initially amorphous alloys also increased with time at room temperature. X-ray diffraction work on the amorphous and crystalline alloys has been started.

3. Deformation and Annealing

3.1 The Effects of Cold Work on the Alloys Mg_3Cd and $MgCd_3$

Personnel: M. B. Bever; J. P. Clark

Only limited data are available on the stored energy of cold work of hexagonal close-packed metals and on most other aspects of their mechanical behavior. Among ordered hexagonal close-packed alloys, information on deformation behavior has been published only for the alloy Mg_3Cd. In our investigation the stored energy of cold work of initially ordered and disordered Mg_3Cd and $MgCd_3$ will be measured. Wire specimens to be deformed in torsion have been prepared. In addition to the stored energy, the heats of formation and the ordering energies will be measured by liquid metal solution calorimetry. Other properties, especially the electrical resistivity and mechanical properties, and the short-range and long-range order will also be investigated.

3.2 Deformation of Face-Centered Cubic Alloys to Very High Strains

Personnel: M. B. Bever; J. F. Breedis; J. W. Pugh

This research is concerned with the effects of deformation on gold-silver alloys at very high strains, the mechanisms of strengthening, dynamic recovery and energy storage and the structural characterization of the deformed alloys. The deformation to very high strains is accomplished by wire drawing. Changes in various properties, in particular mechanical properties and electrical resistivity, will be investigated. The structural characterization of the deformed alloys will involve electron microscopy, measurements of the stored energy and X-ray diffraction. Preliminary experimental work has been carried out.

Publications:

A. K. Jena and M. B. Bever, "On the Temperature Dependence of the Heat of Formation of the Compound AgMg", Trans. TMS-AIME 242, 2367 (1968).

P. Beardmore and M. B. Bever, "The Annealing Behavior of a Gold-Silver Alloy after Deformation at Low Temperatures", Trans. TMS-AIME 245, 165 (1969).

G. Bartsch, "Neutronenbeugungs-Untersuchungen an Cu-Ni-Zn-Legierungen", Z. Metallk. 60, 139 (1969).

A. K. Jena and M. B. Bever, "Enthalpy Interaction Coefficients of Silver, Cadmium, and Gold in Dilute Quaternary Tin-Rich Solutions", Trans. TMS-AIME 245, 1035 (1969).

J. Waldman, A. K. Jena, and M. B. Bever, "The Heats of Formation of Silver-Rich Ag-Cd", Trans. TMS-AIME 245, 1039 (1969).

P. J. Fopiano, M. B. Bever, and B. L. Averbach, "Phase Transformations and Strengthening Mechanisms in the Alloy Ti-6Al-4V", ASM Trans. Quarterly 62, 324 (1969).

A. Gangulee, "On the Solid Solutions of the Quasibinary System PbSe-PbTe", Trans. TMS-AIME 245, 1839 (1969).

A. Gangulee and M. B. Bever, "Effects of Cold Work on Silver-Rich Silver-Magnesium Solid Solution Alloys", Phil. Mag. 20, 519 (1969).

A. K. Jena, J. H. Westbrook, and M. B. Bever, "The Recovery of the Cold-Worked Compound AgMg", ASM Trans. Quarterly 62, 784 (1969).

A. K. Jena, J. H. Smith and M. B. Bever, "On the Dilute Solutions of Gold in Bismuth-Tin Alloys", accepted for publication by Trans. TMS-AIME.

M. B. Bever and C. F. Floe, "Surface Hardening of Steel", article for McGraw-Hill Encyclopedia of Science and Technology.

M. B. Bever, "Metallography", article for McGraw-Hill Encyclopedia of Science and Technology.

M. B. Bever, "Metallurgy", article for the McGraw-Hill Encyclopedia of Science and Technology.

IV. PHYSICAL METALLURGY - Phase transitions in Solids, Coarsening, Radiation Damage, and Condensation in Nozzles

(All personnel from the Department of Metallurgy and Materials Science)

Faculty:

J. W. Cahn, Professor
K. C. Russell, Associate Professor

Graduate Students:

J. C. Goldman, Research Assistant
J. C. Baker, NSF Trainee
S. K. Bhattacharyya, Research Assistant
C. P. Biswas, Research Assistant
P. G. Boswell, Research Assistant
R. B. Heady, Research Assistant
J. Weins, Research Assistant
M. J. Richards, Research Assistant
J. M. Wells, Research Assistant
F. C. Larche, Teaching Assistant
J. Kitler, Graduate Student

Support Staff:

A. M. Santagelo, Technician
S. T. Arsove, Secretary
Martha Finta, Secretary
Kay Fletcher, Secretary

Personnel who have left:

R. B. Heady, now with Shell Development Company, Emeryville, California
J. E. Morral, now at University of Illinois

Degrees Granted:

J. E. Morral, Ph. D. Metallurgy, February 1969
R. B. Heady, Ph. D. Metallurgy, February 1970

Sponsorship:

National Science Foundation, GK-10586, DSR 71384

Office of Naval Research, Nonr-3936 (07), DSR 79809

Advanced Research Projects Agency, SD-90, DSR 75129

National Institutes of Health, DE02384-04, DSR 71552

Sloan Basic Research Fund Grant, 27695

Research Report

1.0 Theory of Spinodal Decomposition

Personnel: J. W. Cahn

Sponsorship: National Institutes of Health

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.

2.0 Electron Irradiation

Personnel: K. C. Russell; J. M. Wells

Sponsorship: Advanced Research Projects Agency

We are proceeding to irradiate iron wires at liquid helium temperatures and deduce the nature of the damage by studying annealing kinetics. We have redesigned the sample mount and heating arrangement so as to obtain rapid heating rates while measuring the sample temperature accurately. Solute-defect trapping is to particular interest to us and we believe analysis of the rate of resistivity decay during annealing will provide informattion on this phenomenon.

3.0 Nucleation and Coarsening in Nozzles

Personnel: K. C. Russell; P. G. Hill; R. Roberts

Sponsorship: Office of Naval Research

We have concluded our investigation of nucleation in supersaturated vapors. We have found that condensation in vapors of NH_3, C_6H_6, $CHCl_3$, and $CFCl_3$ obey the quantum-statistical nucleation rate equation of Lothe and Pound, whereas H_2O and CO_2 vapors are in accord with the 10^{17} times slower nucleation rates predicted by the classical Becker-Doering theory. It is observed that liquids of hydrogen bonded or rod-like molecules generally follow classical theory and all other fluids investigated obey the Lothe-Pound rate equation. This behavior is interpreted in terms of the highly oriented, low entropy surfaces of hydrogen-bonded liquids.

R. Roberts is investigating coarsening of water droplets in a long, slightly divergent supersonic nozzle. Laser light scattering is used to measure droplet size distribution in the 50Å to 1u size range. We want to deduce the mechanism of formation of the micron-size drops frequently observed in turbines under conditions where standard nucleation and coarsening theory predict droplets of 100 - 1000 Å.

4.0 Phase Separation and Crystallization in Glass

Personnel: J. Kitler

Sponsorship: Advanced Research Projects Agency

The Kratky low-angle 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 proportional to the diffuseness to the interface. Expressions giving the form of the Debye correlation function have also been derived.

5.0 Growth Enhancement of Ice Crystals

Personnel: J. Goldman
Sponsorship: National Science Foundation

It is known that when ice solidifies from aqueous solutions, large potentials of the order of hundreds of volts may develop across the solid-liquid interface. This phenomenon is probably responsible for the growth rate enhancements over values for pure water that have been observed. The present research is concerned with evaluating the effects of potential differences on the growth of ice.

6.0 Thermodynamics of Solids Under Non-Hydrostatic Stress

Personnel: F. Larché

Sponsorship: National Science Foundation

The theoretical condition of equilibrium of multi-component solids under non-hydrostatic stress is being investigated. Systems where constraints are imposed on the possible movements of atoms on the lattice are considered. As a future development this work should lead to the formulation of a diffusion equation for specimens under stress.

7.0 Coarsening in Solid State Transformations

Personnel: K.C. Russell, S. Bhattacharyya, and J. Johnson-Weins

Sponsorship: National Science Foundation

The theory of coarsening ("Ostwald Ripening") has been analyzed

in cases where the conditions are quite different from the standard assumptions of the established Lifshitz-Slyozov or Wagner model. The effect of volume fraction of the dispersed phase on its coarsening rate has been considered.

Activation energy for coarsening of compounds has been studied with more emphasis on internally oxidized systems.

At present, research is being done to understand the kinetics of coarsening of dendrite arms in melts.

8.0 Kinetics of Disorder-Order Transitions

Personnel: M. J. Richards

Sponsorship: National Science Foundation

We are investigating the kinetics of disorder-to-order transitions. In conjunction with Mr. Boswell the "pulse-heater" has been rebuilt to allow heat treatments from 0-5000 milliseconds. The system Iron-Palladium has been chosen for study.

9.0 Non-equilibrium Solidification

Personnel: J. Baker

Sponsorship: National Science Foundation

Solidification under conditions far from equilibrium can lead to a spontaneous increase in the chemical potential of the minor component of a binary alloy. Such an experimental result is not inconsistent with thermodynamics, yet there are "thermodynamic" theories that begin by postulating that such solute trapping can't happen. A theoretical and experimental program is aimed at comprehending the nature of the irreversible processes.

10.0 Liquid Phase Sintering

Personnel: R. B. Heady and J. W. Cahn

Sponsorship: National Science Foundation

The capillary forces between particles due to the presence of a liquid phase have been analyzed. Contact geometrics are predicted to have a marked effect on the kinds of interparticle forces and how these depend on liquid volume. The normal force between two spheres is a maximum at infinitesimal liquid volumes, while for the corner-on-plane geometry it is zero and increases rapidly with volume. Sphere contacts have only normal forces, while contacts among jagged particles give rise to shears and torques which are likely to be important in particle rearrangement leading to densification.

11.0 Nucleation Near a Critical Unmixing Point in a Binary System

Personnel: R. B. Heady

Sponsorship: National Science Foundation

To test nucleation theory critical undercooling has been measured in a system in which the thermodynamic functions are known.

12.0 Thermodynamics Near a Critical Unmixing Point in a Binary Liquid System

Personnel: R. B. Heady
Sponsorship: National Science Foundation

Vapor pressure has been determined near the consolute point in the perfluorocyclomethylhexane-cyclomethylhexane system. The thermodynamics function deviates mardedly from those of a regular solution. The scaling law exponents β and γ' have been determined to be $\beta = .33$, $\gamma' = 1.3$

13.0 Massive Transformations

Personnel: K. C. Russell and P. G. Boswell

Sponsorship: National Science Foundation

A double pulse heater has been assembled and is to be used to study the massive transformations in ternary systems. Cu-Zn-X alloys, where X is a small fraction of a third element are being prepared with a view to observing the effect of X on the kinetics of the $\beta \rightarrow \alpha$ massive transformation. Also, the growth rates of massive α inthe equilibrium 2 phase ($\alpha + \beta$) region of the Cu-Zn system are being measured at different temperatures.

Theoretical work is attempting to relate non-equilibrium interphase properties to the growth rate of the phase, with special reference to the presence of third elements, in small amounts, causing interphase boundary drag.

14.0 Heterogeneous Nucleation in Grain Boundaries

Personnel: K. C. Russell and C. Biswas

Sponsorship: National Science Foundation

Experimental investigation was done to study grain boundary nucleation in Cu-Co alloy. The role of excess quenched-in vacancies in nucleation and growth of precipitates will also be studied. The actual mechanism of transport of solute atoms to the precipitates is also under investigation. Finally, we shall attempt to derive a detailed mathematical expression for the kinetics of grain boundary nucleation from these experimental observations.

Theses:

J. E. Morral, "Stability of Ternary Alloys to Continuous Changes of Phase", Ph.D. Thesis, Department of Metallurgy and Materials Science, September 1968.

R. B. Heady, "An Experimental Investigation of Nucleation Theory in a Liquid-Liquid Miscibility Gap", Ph.D. Thesis, Department of Metallurgy and Materials Science, September, 1969

Publications:

J. W. Cahn, "The Metastable Liquidus and Its Effect on the Crystallization of Glass", Journal of the American Ceramic Society, 52, 118, March 1969.

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D. A. Karlyn, J. W. Cahn, and M. Cohen, "The Massive Transformation in Copper-Zinc Alloys", TMS-AIME, 245, February 1969.

J. W. Cahn, "Coherency Stress in Elastically Anisotropic Crystals and Its Effect on Diffusional Processes", Institute of Metals, Monograph and Report Series, 33, 1969

R. B. Heady and J. W. Cahn, "An Analysis of the Capillary Forces in Liquid -Phase Sintering of Spherical Particles", Trans. TSM-AIME, in press.

H. L. Jaeger, E. J. Willson, P. G. Hill, and K. C. Russell, " "Nucleation of Supersaturated Vapors in Nozzles, Part I: H_2O and NH_3", accepted by J. Chem. Physics.

D. B. Dawson, E. J. Willson, P. G. Hill and K. C. Russell, "Nucleation of Supersaturated Vapors in Nozzles, Part II: C_6H_6, $CHCl_3$, and C_2H_5OH", accepted by J. Chem. Phys.

K. C. Russell, "Nucleation on Gaseous Ions", J. Chem. Phys. 50, 1809, (1969).

K. C. Russell, "Comments on Nucleation and Coarsening in Binary Condensed Systems", J. Coll. Interface Sci. 29, 590 (1969).

K. C. Russell, "Nucleation in Solids", in Phase Transformations (1968 Seminar), ASM, Cleveland, in press.

K. C. Russell, "Grain Boundary Nucleation Kinetics", Acta Met. 17, 1123 (1969)

K. C. Russell, "The Role of Excess Vacancies in Precipitation", Scripta Met. 3, 313 (1969).

J. Goldman, H. I. Aaronson and H. B. Aaron, "Growth Mechanisms of Grain Boundary Allotriomorphs in Al-4% Cu at High Homologous Temperature; Interfacial vs. Direct Volume Diffusion", submitted to Trans. AIME.

G. R. Speich and M. J. Richards, "Diffusion Equations for Pearlite Dissolution", TMS-AIME, 245 1073 (1969). (Appendix to paper by G. R. Speich and A. Azirmae).

V. HIGH TEMPERATURE METALLURGY

(Personnel from Department of Metallurgy and Materials Science except where indicated)

Faculty:

N. J. Grant, Professor
R. M. Pelloux, Associate Professor

Research Staff:

W. F. Schilling, DSR Research Staff

Graduate Students:

G. T. Campbell, Research Assistant
W. T. Compton, Research Assistant
J. Cooper, Research Assistant, Naval Architecture
H. M. Dalal, Research Assistant
R. M. Davison, Research Assistant
K. E. Erhardt, Research Assistant
C. H. Jansen, Research Assistant
D. J. Kenton, Research Assistant
M. R. Lebo, Research Assistant
R. Ray, Research Assistant
V. K. Sarin, Research Assistant
M. Singh Grewal, Research Assistant
J. Van den Avyle, Graduate Student
L. F. P. van Swam, Research Assistant
C. P. Weigel, Fellow, Center for Advanced Engineering Study
A. D. Wilson, Research Assistant
S. M. Wolf, Research Assistant

Support Staff:

E. D. Howell, Technician
Lydia White, Secretary

Personnel who have left:

R. Ray, Research Assistant (now at Northeastern University)
C. Weigel, Fellow (returned to Timken Roller Bearing Company)
J. Van den Avyle, Graduate Student (returned to Sandia Corporation)

Degrees granted:

R. Ray, Sc. D., Metallurgy and Materials Science, September 1969

W. Schilling, Sc. D., Metallurgy and Materials Science, June 1969

C. Weigel, S. M., Metallurgy and Materials Science, September 1969

J. Van den Avyle, S. M., Metallurgy and Materials Science, September 1969

A. Wilson, S. M., Metallurgy and Materials Science, June 1969

Sponsorship:

Aeronautical Systems Division, Wright-Patterson AFB, F33615-67-C1441, DSR 70324

National Aeronautics and Space Administration, NGL 22-009-003, DSR 76243

Naval Air Systems Command, Dept. of the Navy, N00019-67-C-0500, DSR 71371

International Copper Research Association, Inc., DSR 71535

National Science Foundation, GK-1374, DSR 70290

Office of Naval Research, Nonr 3963(18), DSR 74621

Advanced Research Projects Agency, SD-90, DSR 78887, DSR 71625

Research Report

1.0 Dispersion Strengthening

Personnel: N. J. Grant; W. Schilling; M. Singh Grewal; S. Wolf, H. Dalal, D. Kenton

Sponsorship: National Aeronautics and Space Administration, Office of Naval Research

Dr. Schilling has demonstrated the applicability of a surface oxidation technique, combined with internal oxidation, to the production of complex oxide-dispersed alloys. The initial work done on Cu-Al-Al_2O_3 alloys is being extended to Ni-base materials. An investigation is underway to correlate the dislocation sub-structure of Fe-BeO alloys with the creep properties. Work is in progress to determine the effect of grain size on creep properties of oxide dispersed Cu-base materials. Earlier work done in this group will be used as a guideline.

Mr. Grewal has produced a series of Ni-BeO alloys by internal oxidation via a fluidized bed technique which exhibit some promising low temperature properties. The high temperature strength and stability of these alloys

are currently being studied.

Mr. Dalal has shown that excess Cr_2O_3 has a profound negative effect on the strength properties of stainless steel-ThO_2 alloys. Alloys have been produced which are nearly free of Cr_2O_3 and show interesting high temperature stress rupture properties. Studies are underway to determine the coarsening kinetics of ThO_2 in these alloys.

Mr. Kenton has initiated a study of carbide dispersed nickel-base alloys. Both mechanical mixing and internal carburization are being used as methods for producing fine dispersions of TiC in a complex Ni-Mo matrix. Simple Ni-TiC alloys, while stronge at room temperature, were unstable at elevated temperatures due to large solubility of TiC in Ni.

Mr. Wolf has attempted to measure the stored energy in oxide dispersed alloys calorimetrically; both iron base and copper base alloys were utilized. To date the equipment has not functioned satisfactorily; the expected precision was not attained in the stored energy values which were measured.

2.0 Development of Chromium Base Alloys

Personnel: N. J. Grant; R. M. Pelloux; Ralph Davison, Alex Wilson, Leo van Swam

Sponsorship: Naval Air Systems Command, Advanced Research Projects Agcy.

The chromium research program is an effort to improve the low temperature ductility, high temperature strength, and the nitrogen resistance of chromium alloys.

Mr. Wilson studied the properties of ternary alloys of Cr-Ru-Ti. Ruthenium lowers the DBTT, ruthenium and titanium raise the recrystallization temperature, and titanium improves the high temperature nitrogen resistance. An alloy containing 10 Ru and 3 Ti seems very promising with a fracture strength of 15,000 psi for 100 hours at 2000 degrees F.

Mr. Davison is using refractory carbide phases (Nb, Ta, Ti, Zr) to raise the recrystallization temperature and improve the ductile to brittle transition temperature. An alloy containing 2% TaC showed 6% uniform elongation at room temperature but failed by cleavage. The same alloy does not show a sharp transition temperature for ductility, which suggests that it could be used at room temperature. Mr. Davison is also studying the influence of grain size on the ductile-brittle transition temperature of pure chromium since Hahn reported that coarse grained chromium has a lower transition temperature than fine grained chromium. Preliminary tests have shown that it is possible to produce a grain size of about 2 microns after the recrystal-

lization treatment.

Mr. van Swam is presently studying Cr-Ru-Ti alloys with a dispersion of thoria particles. The main problem at the moment is to reduce the chromium oxide formed during communition and mixing of the powders.

3.0 Rapid Quenching (Splat Cooling) on Alloy Structure and Properties

Personnel: N. J. Grant; R. M. Pelloux; C. Jansen, M. Lebo, R. Ray, V. Sarin

Sponsorship: National Aeronautics and Space Administration, International Copper Research Association, National Science Foundation

The structure and the properties of rapidly quenched alloys are being investigated. Cooling rates from the liquid state are of the order of 10^4 to 10^5 degrees C per second for an apparatus which produces pound-lot quantities of splat cooled materials suitable for consolidation and bulk testing. When small (15 mg) thin foils are produced, cooling rates up to 10^9 degrees C per second can be achieved. The main goals of the research program are centered around:

a) increases in solid solubility
b) formation of new metastable phases
c) formation of amorphous and microcrystalline phases
d) production of ultra-fine grained (or dendritic) structures
e) control of excess phases in terms of particle size and distribution
f) change of the microstructure of non-equilibrium phases during subsequent decomposition by working or annealing.

Dr. Ray completed a study of ten splat-cooled binary alloy systems of transition metals. He found $TiFe_3$, a new metastable crystalline phase, and new microcrystalline phases in Ti-Cu, Zr-Cu, Zr-Ni, Zr-Co, Zr-Fe, Zr-Pd, and Zr-Mn. Defect structures containing up to 25 atomic percent vacancies were discovered in Ti-Ni and Ti-Co. Large increases in solid solubility were observed in almost all of the systems studied.

Mr. Sarin is studying copper alloys containing 0.1 to 1.0 wt. % Zr prepared over a wide range of quenching rates (10^2 to 10^8 degrees/sec) in order to vary the microstructures and solubilities. It is expected that a significant improvement in high temperature strength and stability will be achieved.

The decomposition behavior of splat-cooled aluminum alloys containing Mn, Fe, Co, Ni, Cu, or Pd is being studied by Mrs. Jansen. As-quenched

and annealed splat foils are examined by X-ray diffraction and transmission electron microscopy. In particular, the decomposition of Al-Fe supersaturated alloys will be followed for potential use as dispersion strengthened alloys; and Al-Cu supersaturated alloys for aging phenomena.

Mr. Lebo is producing pound lots of splat-cooled aluminum-silicon alloys in an attempt to produce a fine dispersion of silicon in aluminum. Mechanical properties are of interest. The commercial alloy, 2024 aluminum, was produced by splat cooling and resulted in a very fine distribution of intermetallic particles with important benefits in yield strength and low cycle fatigue resistance.

4.0 Fatigue Behavior of Aluminum Alloys

Personnel: R. Pelloux; N. J. Grant; K. Erhardt, J. Van den Avyle, J. Cooper

Sponsorship: Air Force Materials Laboratory, Advanced Research Projects Agency

Mr. Erhardt has studied, by means of replica and scanning electron microscopy, the mechanisms of crack initiation in a 2024-T4 aluminum alloy. At all strain amplitudes the cracks initiate at intermetallic inclusions. At large strain amplitudes the stage-I crack follows the slip bands resulting from the large plastic strains associated with the inclusions. The low strain fatigue cracks remain essentially normal to the major tensile axis even in the early stages of propagation. Stage-I was clearly identified by means of scanning electron microscopy and it extends over two or three grains below the surface. The inclusions do not play any role during Stage-I beyond the initiation stages.

Mr. Van den Avyle studied the effects of intermetallic inclusion sizes on the fatigue properties of 2024-T4 aluminum. Air atomized and splat cooled materials were extruded to form alloys which possessed very small constituent particles (less than 1 micron) compared to the commercial alloy (up to 20 microns). The extruded alloys showed a large improvement in f fatigue life near the endurance limit in spite of a coarse grain size. Currently work is in progress to refine the grain size by cold working after extrusion and to limit longitudinal delamination by varying the extrusion ratio.

Mr. Cooper has started a program to study the influence of aging of an Al-Zn-Mg alloy (7075) on the fatigue properties in a sea water corrosive environment. The endurance limits and the crack propagation rates will be

related to the stability of the microstructure.

5. Deformation and Fracture at Hot Working Temperatures

Personnel: N. J. Grant; R. M. Pelloux; G. Campbell, W. Compton, C. Weigel

Sponsorship: Advanced Research Projects Agency

Mr. Campbell has completed a study of the hot plasticity of an as-cast 18-11 type stainless steel with high nitrogen content. It was found that a nitride precipitate at the grain boundary greatly reduced hot plasticity of this material. Recrystallization of the cast structure induced by low temperature deformation and a high temperature anneal was found to triple the hot plasticity. Recrystallization studies performed on the same material after the initial cold work - annealing sequence showed that the efficiency of a given plastic strain increment to produce a given reduction in grain size strongly depends on the strain rate. The higher strain rates of hot working were found to be as efficient as cold working with regards to recrystallization behavior.

The recrystallization behavior of a cast, vacuum arc melted 18-8 alloy is being studied in detail as a function of 1) the amount of plastic strain; 2) strain rate; 3) temperature; and 4) holding time after each straining step.

Mr. Weigel has completed a study on a low alloy steel (AISI 4130) treated with minor additions of Ti, Cb, V, and Al to control the grain size. This study, which is related to the high temperature forging behavior of the alloy, showed that the addition of aluminum led to a transition from transgranular to intergranular fracture and a lower ductility at low strain rates in the temperature range from 1700 to 1900 degrees F. The alloys treated with Ti, Cb, and V maintained a uniform ductility over the wide temperature and strain rate ranges investigated.

Mr. Compton is studying the hot plasticity of Fe-W-C alloys with the aim of achieving extreme grain refinement. The resultant properties of these alloys are of interest.

Theses:

R. Ray, "Splat Cooling of Binary Alloys of Transition Metals", Sc. D. Department of Metallurgy and Materials Science.

W. F. Schilling, "Dispersion Strengthened Alloys Produced by a

Surface Oxidation Technique", Sc. D., Department of Metallurgy and Materials Science.

J. A. Van den Avyle, "Structure of Refinement in Fatigue Life of Aluminum Alloys", S. M., Department of Metallurgy and Materials Science.

C. P. Weigel, "The Influence of Grain Growth Inhibitors on the High Temperature Ductility of Low Alloy Steel", S. M., Department of Metallurgy and Materials Science.

A. D. Wilson, "Properties and Behavior of Cr-Ru-Ti Ternary Alloys", S. M., Department of Metallurgy and Materials Science.

Publications:

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C. Jansen, B. C. Giessen, N. J. Grant: "Atmospheric Corrosion of Splat Cooled Aluminum Alloy Foils", Jour. Metals, Dec. 1968, p. 10.

P. K. Srivastava, B. C. Giessen, N. J. Grant: "New Metastable Electron Phases in Binary B-Metal Alloys", Acta Met., V. 16, Oct. 1968, p. 1199.

B. C. Giessen, R. Wang, N. J. Grant: "New A_3B_5 Phases of the Titanium Group Metals with Rhodium", Trans. Met. Soc. AIME, 245, June 1969, p. 1207.

K. Erhardt, N. J. Grant: "Behavior of 2024 Aluminum in Low Cycle Fatigue at Low Strain Rates as a Function of Temperature". Fracture 1969; Proc. of the 2nd International Conference on Fracture, Brighton, April, 1969; Chapman & Hall, Ltd.

W. F. Smith and N. J. Grant: "Mechanism of Formation of Precipitate-Free Zones in an Al-4.7% Zn - 3.9% Mg Alloy", Trans. ASM, 62, 1969, 724.

Pelloux, R. M.: "Mechanisms of Formation of Ductile Fatigue Striations", Trans. ASM, V. 62, 1969, p. 281.

Pelloux, R. M.: "Corrosion Fatigue Crack Propagation", Proc. of 2nd International Conference on Fracture, Brighton, April, 1969; Chapman & Hall, Ltd.

VI. PROCESS METALLURGY AND HIGH-TEMPERATURE CHEMISTRY

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

J. F. Elliott, Professor
T. B. King, Professor
B. H. Rosof, Assistant Professor

Research Staff:

J. Chipman, Professor Emeritus
T. Engh, Research Fellow
H. Wada, DSR Research Staff
T. Wada, DSR Research Staff
T. Yasuda, Visiting Scientist
J. Dilewijns, Visiting Scholar

Graduate Students:

D. Baty, Research Assistant
C. Douglas, Research Assistant
H. Fine, Research Assistant
C. Finn, Research Assistant
M. Ikeda, Graduate Fellow
M. Maulvault, Research Assistant
H. Pielet, Research Assistant
G. Sigworth, Graduate Fellow
P. Tichauer, Research Assistant
A. Washburn, Graduate Fellow
J. Wright, Research Assistant
J. Yavorsky, Research Assistant

Support Staff:

E. N. Bradbury, Technician
S. M. Grenier, Secretary
D. R. Mountain, Secretary

Personnel who have left:

A. Briskine (Returned to Paris, France)
T. Kuwabara (Returned to Fuji Iron & Steel, Ltd., Japan)
F. Larché (Transfered to Physical Metallurgy, Prof. Cahn)
J. Nichols (Left because of ill health)
M. Onillon (Returned to IRSID, Metz, France)
J. Popper (Now at Sloan School of Management, M.I.T.)
H. Sakao (Returned to Nagoya University, Japan)

Degrees Granted:

A. Briskine, M.S., Chemical Metallurgy, August 1969
T. Kuwabara, M.S., Chemical Metallurgy, June 1969
J. Popper, M.S., Chemical Metallurgy, August 1969

Sponsorship:

American Iron & Steel Institute, Contract Numbers 39-194, 39-195, 30-218, 30-219; DSR 71115-6-7-8, 71120
American Iron & Steel Institute, Contract 68-164, DSR 70542
American Iron & Steel Institute, Contract 146, DSR 70544
American Metal Climax Foundation Fellowship
Union Carbide Corp., Carbon Products Division, DSR 71299
Copperweld Steel Company, DSR 71969
Fuji Iron & Steel Co., Ltd., Japan; Fellowship
Hitachi Research Ltd.
United States Army, DAHC 04-67-C-0036, DSR 70368

Research Reports:

1.0 Physico-Chemical Properties of Sulfides

Sponsorship: American Iron and Steel Institute, and Hitachi Research, Ltd.

Currently equipment is being set up to measure surface and interfacial tensions in the Fe-O-S and Fe-Mn-S systems. The experimental techniques will be the maximum bubble drop method, grain boundary grooving and a modification of the du Nuoy method. Mr. Yasuda and Mr. Douglas are making preliminary measurements on the Pb-Zn system early in 1970.

2.0 Problems in Heat and Mass Transfer

Sponsorship: American Iron and Steel Institute; Carbon Products Division, UCC and Fuji Iron and Steel Co., Ltd., Japan

This year Dr. Engh has devoted his time to an intensive analysis of the role that slag may play as a heat transfer medium in steelmaking systems. He has been measuring the "effective" thermal conductivity of several typical slags between 1200 and 1550°C. Mr. Fine is continuing this type of measurement but with much refined equipment.

Mr. Yavorsky is now obtaining measurements of temperatures in the electrodes of large commercial electric steel furnaces. He is using these measurements to test the validity of the mathematical model that he has developed to describe the temperatures and heat flow in the electrodes.

Measurements of the temperatures in the electrode, slag and ingot of an experimental electroslag remelting system are now proceeding satisfactorily. Mr. Maulvault has solved a number of experimental difficulties this winter and he now is ready to apply his experimental results to the evaluation of the physical parameters of importance to heat flow in the system.

Mr. Ikeda is exploring the effects of the conditions of heat flow on the manner in which a solid dendrite grows into the liquid during the process of solidification.

Mr. Sigworth is proceeding with the development of an electrochemical method for determining the rate at which oxygen and a deoxidizing element combine in liquid steel.

In his study of convective motion of the interdendritic liquid in a partially solidified liquid, Mr. Pielet has completed his work on the Al-4% Cu alloy and is now working with alloys in the Fe-Ni system.

3.0 Thermodynamic Properties of Alloys

Sponsorship: American Iron and Steel Institute, Army Research Office - Durham

Doctor's T. and H. Wada are determining the thermodynamic properties of carbon in alloyed austenite. It is hoped that the systems Fe-Ni-C, Fe-Mn-C and Fe-Si-C can be completed this year.

Dr. Dilewijns is continuing the determination of the activity of silicon in various silicon bearing phases that was begun by Professor Sakao last year. With a somewhat modified experimental method, he has checked the earlier results on Fe-Si alloys and now is measuring the free energy of formation of silicon carbide.

4.0 Structure of Liquid Complex Oxides

Sponsorship: American Iron and Steel Institute

Mr. C. Finn has made further progress in his study of the structure of phosphate melts containing up to 15 mol/% SiO_2. It has been definitely confirmed that silicon enters phosphate chains present in the molten silico-phosphate at the center and this process continues until all phosphate chains have been severed by the incorporation of silicon. The experimental method used cannot shed any light on the incorporation of further silica into the phosphate melt. The work is continuing with a study of the effect of alumina on the distribution of polymolecules in silico-phosphate melts.

5.0 Electrochemical Processes in Steelmaking

Sponsorship: American Iron and Steel Institute

Mr. P. Tichauer has constructed apparatus for applying the galvanostatic method to the study of electrode reaction kinetics in high temperature melts. The work so far has demon-

strated that, in high temperature systems, transition times become very long particularly where liquid electrodes are used. The interpretation of results is, therefore, complicated by convection in the melt. Studies have been made with solid electrodes in both oxide and halide melts and further attempts will be made to use a liquid electrode. It is hoped eventually to study the reactions involving the charging and discharging of sulphur at a liquid electrode which is contaminated by dissolved oxygen. These measurements are of interest in electroslag remelting processes.

6.0 Deoxidation Reactions in Steels

Sponsorship: American Iron and Steel Institute and Copperweld Steel Corporation

Mr. Baty has begun a study of the influence of the process of solidification on the morphology of the oxides of iron and aluminum in Fe-O-Al alloys. His initial experiments are with levitated melts of the alloys to avoid interference from crucible materials. This work is supervised jointly by Professors Flemings and Elliott.

The relationships between the process of segregation and deoxidation products and gas generation in commercial steels is being studied by Mr. Wright.

Publications:

A. Ghosh and T. B. King, "Kinetics of Oxygen Evolution at a Platinum Anode in Lithium Silicate Melts", Trans., TMS-AIME, Vol. 245, January 1969.

T. B. King, "Kinetics of Desulphurization of Cast Iron by Slags" RECENT RESEARCH ON CAST IRON, ed. H. D. Merchant, Gordon and Breach, Science Publishers, Inc., 1968, p. 617.

F. E. Woolley and J. F. Elliott, "Mathematical Models of a Transient Thermal System", TMS-AIME Vol. 245, pp. 1765-1773, 1969.

S. Ban-ya, J. F. Elliott and J. Chipman, "Activity of Carbon in Fe-C Alloys at 1150°C", Trans., TMS-AIME, 1969, Vol. 245, pp. 1199-1206.

H. G. Hadrys, M. G. Frohberg and J. F. Elliott, "Activities in the Liquid Fe-Cr-C(sat), Fe-P-C(sat) and Fe-Cr-P Systems at 1600°C", Submitted to Trans., TMS-AIME.

J. F. Elliott and J. Yavorsky, "Heat Flow in an Arc Furnace Electrode--A Computer Study", 73rd Casting Congress, Submitted to Trans., American Foundrymen's Society.

S. Ban-ya, J. F. Elliott and J. Chipman, "Thermodynamics of Austenitic Fe-C Alloys", Submitted to Trans., AIME.

G. Forward and J. F. Elliott, "Formation of Silica and Silicates During the Solidification of Fe-Si-O Alloys", Submitted to Trans., AIME.

S. Ban-ya and J. Chipman, "Sulfur in Liquid Iron Alloys II: Effects of Alloying Elements", Trans., TMS-AIME, Vol. 245, pp. 133-143, January 1969.

S. Ban-ya and J. Chipman, "Sulfur in Liquid Iron Alloys III: Multicomponent Systems", Trans., TMS-AIME, Vol. 245, pp. 391-396, February 1969.

VII. SURFACE CHEMISTRY

(All Personnel from Department of Metallurgy and Materials Science)

Faculty:

P. L. deBruyn, Professor

Research Staff:

F. Z. Saleeb, Research Associate

Graduate Students:

J. Drummond, Graduate Student
H. Hassan, Research Assistant
J. S. Hoch, Graduate Student
B. D. McLaughlin, NSF Trainee
J. W. Morris, NSF Trainee
M. Reverdy, Research Assistant
G. Sheldon, Research Assistant

Support Staff:

Patricia E. Gavagan, Secretary

Personnel who have left:

J. S. Hoch
B. D. McLaughlin
J. W. Morris
M. Reverdy

Degrees Granted:

J. S. Hoch, SM, Metallurgy, June 1969
B. D. McLaughlin, Ph. D, Metallurgy, September, 1969
J. W. Morris, Ph. D, Metallurgy, February 1969
M. Reverdy, SM, Metallurgy, September 1969

Sponsorship:

Department of Health, Education, and Welfare, P. H. S. IROI DE02769-01 DEN

Research Report

1.0 Influence of the Structure and Composition of Clean Solid Surfaces on the Nature and Behavior of Solid-Fluid Interfaces

Personnel: P. L. deBruyn; J. S. Hoch

Sponsorship: None

The study of the interface NiO(s)/aqueous solution and Ni(OH)2/aqueous solution has been continued with an attempt to understand the kinetics of the establishment of the electrical double layer. A brief study was also made of the interface between lead dioxide and aqueous electrolyte solutions. The two experimental techniques used were adsorption measurements of potential-determining ions (H^+, OH^-) and a. c. surface impedance measurements. Quantitative comparison of the values of the capacitance obtained from the two methods was limited to the order of magnitude agreement because of uncertainty in surface area of lead dioxide precipitate and surface roughness of the PbO_2 electrodes in the a. c. measurements.

2.0 Kinetics and Mechanism of Hydroxyapatite Dissolution

Personnel: P. L. deBruyn, H. Hassan, M. Reverdy, F. A. Saleeb, G. Sheldon

Sponsorship: Department of Health, Education, and Welfare, P. H. S.

The growth, dissolution and transport properties of hydroxyapatite [$(Ca_{10}(OH)_2(PO_4)_6$] and related materials will be studied. At present, attempts are being made to measure the diffusion of Sr^{++}, Ca^{++}, F^- in single crystals of hydroxy and chlorapatite. A study of the sintering and crystallization behavior of compacted powders at various temperatures and atmospheres is being initiated. In addition, materials are being prepared to determine the surface behavior of fine apatite particles in aqueous solutions by means of electrophoretic measurements.

Theses:

J. S. Hoch, "Kinetics of Adsorption on Nickel Oxide Surfaces in Aqueous Solution," June 1969.

J. W. Morris, Jr., "On the Continuum Thermomechanics of Two-Phase Interfaces," February 1969.

B. D. McLaughlin, "The Dynamics and Thermodynamics of Solid-Fluid-Fluid Three-Phase Contact," September 1969.

M. R. Reverdy, "High Temperature Study of Hydroxyapatite," September 1969.

Publications:

B. D. McLaughlin and P. L. deBruyn, "The Dynamics and Thermodynamics of Solid-Fluid-Fluid Three-Phase Contact," J. Colloid and Interface Science, Vol. 30, No. 1, May 1969.

VIII. METALS PROCESSING - CASTING AND SOLIDIFICATION

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

M. C. Flemings, Professor

Research Staff:

T. Z. Kattamis, Research Associate
R. Mehrabian, Research Associate
S. N. Singh, Research Associate
E. H. Backman, Foreman
W. A. Brown, DSR Research Staff
R. G. Riek, Technical Instructor

Graduate Students:

D. Apelian, Teaching Assistant
M. Basaran, Graduate Student
D. L. Baty, Research Assistant
L. K. Bigelow, Research Assistant
W. E. Brower, Research Assistant
A. J. Campagna, Research Assistant
D. S. Gnanamuthu, Research Assistant
M. A. Keane, Teaching Assistant
S. A. Metz, Research Assistant
M. Myers, Research Assistant
E. S. Palmer, Teaching Assistant
M. D. Rinaldi, Teaching Assistant
A. M. Reti, Research Assistant
F. M. Schlecht, Graduate Student
D. R. Spencer, Research Assistant
J. C. Yarwood, Research Assistant

Support Staff:

R. A. Berry, Technician
A. J. Zona, Engineering Assistant
A. Barbara Rich, Secretary

Degrees Granted:

R. Mehrabian, Sc.D., Metallurgy, February 1969 (to Research Staff, MIT)

J. C. Yarwood, Sc.D., Metallurgy, February 1969 (to Olin Mathewson Corp.)

W. E. Brower, Sc.D., Metallurgy, June, 1969 (to Montsanto Chemical Corp.)

Sponsorship:

Army Materials Research Agency, DAAG-46-68-C-0043, DSR 70811

Army Materials Research Agency, DAAG-46-68-C-0044, DSR 70812

Army Material Command, DAAG-25-69-C-0489, DSR 71454

Office of Naval Research, NONR-3963(09), DSR 79988

American Foundrymen's Society, DSR 70438

Advanced Research Projects Agency, DSR 78893

American Iron and Steel Institute, DSR 76379

American Iron and Steel Institute, DSR 71119

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 (ARPA)

Continuing progress has been made in establishment of the Metal Crystal Growth Facility as part of the Center for Materials Science and Engineering. This facility is described separately. Research on crystal growth has included continuation of study of growth of "composite" crystals and study of crystals grown under conditions of extremely vigorous fluid flow.

2.0 Effect of Fluid Flow on Structure; Composite Materials (ONR)

Research has recently been completed on effects of convection on perfection of directionally solidified eutectic alloys. Current related work is on solidification, with a "composite" eutectic-like structure, of aluminum alloys that are far from eutectic composition. Work is on binary aluminum-copper alloys and on ternary aluminum-copper-nickel alloys.

Other work on convection includes a study of effect of extremely vigorous convection on solidification structure. Apparatus has been designed and constructed to achieve velocity gradients at a solidifying liquid-solid interface the order of 10^5/sec. These gradients are far

in excess of those obtained in any previous solidification study. Experiments show significant influences of the flow on structure.

3.0 Macrosegregation (AISI, ONR)

This research comprises analytical and experimental study of macrosegregation in ingot solidification. Results of this program show that most, if not all, commercially important types of macrosegregation in castings and ingots result from a single basic cause. That cause is flow of solute-rich liquid between dendrites in the liquid-solid region of the partially solidified casting or ingot. Driving forces for the flow are solidification contraction, thermal contractions of liquid and solid, and gravity acting on fluid of variable density.

4.0 Inclusions (Army, AISI)

Several related activities are under way, designed to study the formation and growth of non-metallic inclusions in metal melts (especially in steel). Inclusion nucleation and growth is being studied in a number of ternary iron base alloys including Fe-S-O, Fe-Si-O, Fe-Mn-S, and low alloy steel. Inclusion "pushing", coalescence, and ripening are being studied. Effects are being examined of high temperature homogenization treatments on morphology of inclusions in cast steel. Also being studied is influence of inclusion morphology and chemistry on mechanical properties.

5.0 Ultra-High Strength Aluminum Alloys (Army)

Influence of solidification heterogeneities on properties of wrought aluminum alloys is being studied in this program. It has been shown that by careful control of solidification and thermo-mechanical processing significant improvements in properties of wrought aluminum alloys can be obtained. Ductility of existing alloys, especially in the transverse directions, is increased several fold. Fracture behavior of the aluminum alloys is studied with the scanning electron microscope and related to solidification and subsequent processing.

6.0 Hot Tearing (American Foundrymen's Society)

Work is being conducted on influence of solidification variables on "hot tearing" (tendency of alloys to rupture during solidification). Experimental apparatus has been designed and is in use to strain partially solid alloy castings at known rates and temperatures.

7.0 Heat Flow in Alloy Solidification (Army)

A study is being made of heat flow in solidification of alloys that solidify over a wide temperature range. Study is both theoretical, using numerical analysis procedures for solution, and experimental. Aim is to optimize local cooling rate at critical temperatures during ingot solidification so as to minimize local dendrite arm spacing.

8.0 Metal Filtration (Army)

Small, solid impurity particles are known, or thought, to be present in many metallic alloys, even those of very high purity. Estimates range as high as 10^7 particles per cubic centimeter. In this work, fine filters are employed to remove as many of these particles as possible (from molten aluminum alloys). Solidification behavior, structure, and properties of the filtered material are studied.

Theses:

R. Mehrabian, "Macrosegregation", Sc.D. Thesis

J. C. Yarwood, "Inclusion Formation in the System Fe-FeO-FeS", Sc.D. Thesis

W. E. Brower, "Solidification-Structure-Fracture Relations in Inclusion Bearing Iron", Ph.D. Thesis

Publications:

M. C. Flemings, R. Mehrabian, G. E. Nereo, "Macrosegregation, Part II", Trans. Met. Soc. AIME, 242, pp. 41-49, 1968.

M. C. Flemings, G. E. Nereo, "Macrosegregation, Part III", Trans. Met. Soc. AIME, 242, pp. 50-55, 1968.

M. C. Flemings, "Directional Solidification and Composite Structures", Surfaces and Interface II, Ed. J. Burke et al, Syracuse University Press, pp. 313-352, 1968.

M. C. Flemings, "Application of Solidification Theory to Large Castings and Ingots", The Solidification of Metals, J.I.S.I., Publication 110, pp. 277-288, 1968.

M. C. Flemings, "Casting Metals", Science and Technology, pp. 13-24, December, 1968.

S. N. Singh, M. C. Flemings, "Influence of Ingot Structure and Processing on Mechanical Properties and Fracture of a High Strength Wrought Aluminum Alloy", Trans. Met. Soc. AIME, 245, pp. 1811-1819, 1969.

Accepted for Publication:

M. C. Flemings, D. R. Poirier, R. V. Barone, H. D. Brody, "Microsegregation in Iron Base Alloys", J. Iron and Steel Institute.

T. F. Bower, S. N. Singh, M. C. Flemings, "Development of High Strength Wrought Aluminum-Base Alloys", Trans. Met. Soc. AIME.

R. Mehrabian, M. C. Flemings, "Laboratory Simulation of the Negative Cone of Segregation", Trans. Met. Soc. AIME

R. Mehrabian, M. C. Flemings, "Macrosegregation in Ternary Alloys", Trans. Met. Soc. AIME.

S. A. Metz, M. C. Flemings, "Hot Tearing in Cast Metals", Trans. A.F.S.

IX. CORROSION LABORATORY

Faculty:

H. H. Uhlig, Professor, Metallurgy and Materials Science

Research Staff:

(Mrs.) Sultana Stancu-Ciolac, Guest of the Institute, Metallurgy and Materials Science

Graduate Students:

H. H. Lee, Research Assistant, Metallurgy and Materials Science

T. M. Murphy, Research Assistant, Metallurgy and Materials Science

R. T. Newberg, Research Assistant, Metallurgy and Materials Science

R. W. Revie, Research Assistant, Metallurgy and Materials Science

A. W. Swanson, National Steel Corp. Fellow, Metallurgy and Materials Science

Support Staff:

Constance C. Lowery, Secretary, Metallurgy and Materials Science

Personnel who have left:

T. M. Murphy, Research Assistant, Metallurgy and Materials Science (Now at Sikorsky Aircraft)

Degrees Granted:

T. M. Murphy, S.M., Metallurgy and Materials Science, August 1969

Sponsorship:

Army Research Office-Durham, DA-31-124-ARO(D)-47, DSR 79341

Office of Saline Water, Grant 14-01-0001-1133, DSR 71507

Shell Companies Foundation, DSR 70816

American Iron and Steel Institute, DSR 70436

Inland Steel Fellowship, DSR 71140

National Steel Fellowship, BA 21930

Research Report

1.0 Pitting Corrosion (OSW)

Measurements and interpretation of critical potentials below which corrosion pitting of copper-nickel alloys does not occur. Effect of environmental and metallurgical factors.

2.0 Stress Corrosion Cracking (AROD)

Critical experiments to differentiate between various proposed mechanisms. Measurement and interpretation of critical potentials below which cracking does not occur. Effect of environmental and metallurgical factors on critical potentials and cracking susceptibilities mostly of carbon and stainless steels.

3.0 Hydrogen Cracking (AROD)

Effect of cold work and composition on susceptibility of alloy steels.

4.0 Corrosion Fatigue (AISI, Inland Steel)

Effect of stress, heat treatment, chloride ion concentration, dissolved oxygen, pH and applied potential on corrosion fatigue of low- and high-strength steel. Measurement of the critical corrosion rate below which the environment is no longer a factor.

5.0 Passivity (Shell)

Effect of alloyed electron donors (non-transition elements) and of electron acceptors (transition metals) on critical composition for passivity of Cu-Ni alloys as measured potentiostatically in sulfuric acid. Structure of the passive film.

6.0 Thin Film Oxidation Kinetics (National Steel)

Oxidation rates of various faces of single crystal copper follow two-stage logarithmic kinetics. Gaseous pretreatment in nitrogen or

hydrogen has a large effect on oxidation rates. The results are interpreted in terms of oxide space charge, work functions, and surface faceting.

Theses:

T. M. Murphy, "Effect of Heat Treatment on Stress Corrosion Cracking of 4140 Steel," S.M., Department of Metallurgy and Materials Science, August 1969.

Publications:

H. H. Uhlig, "An Evaluation of Stress Corrosion Cracking Mechanisms," Proc. of "Fundamental Aspects of Stress Corrosion Cracking," Ohio State University, September (1968).

H. H. Uhlig and E. W. Cook, Jr., "Mechanism of Inhibiting Stress Corrosion Cracking of 18-8 Stainless Steel in $MgCl_2$ by Acetates and Nitrates," J. Electrochem. Soc. 116, 173-177 (1969).

H. H. Uhlig, "Reply to 'Uhlig Model of Logarithmic Oxidation' by B. Chattopadhyay and J. Measor," Scripta Metallurgica 3, 75-76 (1969).

H. H. Uhlig, "Answer to 'The Uhlig Defect Model of Oxidation Kinetics' by A. T. Fromhold, Jr." J. Electrochem. Soc. 116, 455-457 (1969).

H. Böhni and H. H. Uhlig, "Effect of Alloyed Re on the Critical Pitting Potentials of 18% Cr-10% Ni Stainless Steels," Corrosion Science 9, 353-355 (1969).

H. Böhni and H. H. Uhlig, "Environmental Factors Affecting the Critical Pitting Potential of Aluminum," J. Electrochem. Soc. 116, 906-910 (1969).

F. Mansfeld and H. H. Uhlig, "Effect of d-Band Structure on Secondary Passivity in Ni-Cu Alloys, " Corrosion Science 9, 377-384 (1969).

H. Uhlig and D. Duquette, "Alleged Stress-Corrosion Cracking of Pure Cu," Corrosion Science 9, 557-560 (1969).

X. ELECTRONIC MATERIALS LABORATORY

(Personnel from the Department of Metallurgy and Materials Science except where indicated)

Faculty:

H. C. Gatos, Professor
A. F. Witt, Associate Professor

Research Staff:

M. Lichtensteiger, DSR Research Staff
S. Minagawa, Visiting Scientist

Graduate Students:

C. L. Balestra, Research Assistant
J. J. Daniele, Graduate Student
G. T. Galyon, General Telephone & Electronics Fellow
I. Lagnado, Graduate Student
D. C. Miller, Research Assistant
J. A. Mcrozkowski, Teaching Assistant
K. Owyang, Graduate Student
N. S. Platakis, Research Assistant
J. M. Sandor, Research Assistant
O. Sandven, Graduate Student
R. Singh, Research Assistant
S. Spitzer, Graduate Student, Electrical Engineering
A. M. Vejux, Research Assistant
B. W. Wessels, Teaching Assistant

Support Staff:

W. J. Fitzgerald, Engineering Assistant
C. J. Herman, Engineering Assistant
J. Gricci, Technician
Sue C. Jett, Secretary
Pamela B. Polzen, Secretary

Degrees Granted:

H. I. Andrews III, Ph. D., Metallurgy, June 1969
Iyer Subramanian, S. M., Electrical Engineering, June 1969
P. H. Bellin, Ph. D., Metallurgy, February 1969
J. M. Harris, Ph. D., Metallurgy, June 1969
L. C. Kimerling, Ph. D., Metallurgy, February 1969
L. Kiss, S. M., Metallurgy, February 1969
T. M. Valahas, Ph. D., Metallurgy, February 1969
Marilyn Tamm, S. B., Metallurgy, June 1969

Personnel who have left:

J. T. A. Pollock, DSR Research Staff (Now at Tyco Laboratories, Waltham, Massachusetts)
M. Nemeth, Visiting Scientist
T. Nemeth, Visiting Scientist
P. H. Bellin, Research Assistant (Now at Philips Laboratories, Briarcliff Manor, N. Y.)
J. M. Harris, IBM Fellow (Now at IBM Research Institute, Fishkill, N. Y.)
L. C. Kimerling, Research Assistant (Now at Air Force Cambridge Research Laboratories, Bedford, Massachusetts)
L. Kiss, Graduate Student (Now at Central Scientific Laboratory, Richmond, Victoria, Australia)
T. M. Valahas, Research Assistant (Now at Research Center of National Defense, Athens, Greece)
H. I. Andrews III, Research Assistant (Now at Honeywell Inc., Lexington, Massachusetts)

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75122, 75126, 78896
National Aeronautics and Space Administration, NGR22-009-125, DSR 76335
National Aeronautics and Space Administration, NsG-496, DSR 76188
Office of Naval Research, Nonr 3963(05), DSR 79540
National Science Foundation GK-1653, DSR 71474
Wright-Patterson Air Force Base, F33 615-69-C-1031, DSR 71300

Research Report

1.0 Semiconductor Surfaces

Personnel: H. C. Gatos, A. F. Witt; C. L. Balestra, T. M. Valahas, J. M. Harris, S. Spitzer

Sponsorship: Office of Naval Research and Advanced Research Projects Agency

The work on gallium arsenide field effect measurements has shown that the field induced disturbance of the equilibrium between the surface states and the bulk is reestablished by thermal excitation of majority carriers over the surface potential barrier. The dependence of the characteristic time constant upon temperature enables evaluation of the activation energy of the process. Under illumination the minority carriers become extremely important in the surface conductance; and the process becomes essentially independent of temperature.

The field effect and other electrical measurements on high energy gap semiconductors have been continued. Pulsed field effect measurements on mechanically polished cadmium sulfide were made over a range of temperatures from 77°K to 300°K. No detectable signal was obtained. It became apparent that "clean" surfaces were needed for the investigations. Accordingly a device for cleaving under ultra-high vacuum has been designed and constructed. It can be employed in conjunction with contact potential measurements employing the vibrating electrode technique. Preliminary field effect measurements have been carried out on p- and on n-type high conductivity silicon carbide at 77°K and 300°K. A weak decay of the order of 50 microseconds was found at room temperature. Similar experiments will be conducted at higher temperatures on samples of lesser carrier concentration.

Regarding the electronic configuration of InSb surfaces described in previous reports it is of interest to note that recent publications from other research groups have confirmed our original conclusion that the surface states which were considered in our work are intrinsic rather than extrinsic.

In the course of studying the epitaxial growth of silicon carbide it became necessary to develop a reliable and simple technique for identifying the (0001) and the $(000\bar{1})$ surface of hexagonal silicon carbide. An alkaline solution of $K_3Fe(CN)_6$ has been developed which at approximately 100°C differentiates reproducibly between

the two surfaces. The silicon surface develops etching patterns, the intensity of which depends on the length of the etching. In contrast the carbon surface remains essentially unattacked. Regarding the high temperature surface behavior of silicon carbide it was found that the etchingrate of the alpha (hexagonal) modification in hydrogen at temperatures above 1550°c depends on the susceptor material on which the inductively heated silicon carbide rests. Molybdenum exhibited the most pronounced effect increasing the etching rate by about one order of magnitude over that of all other susceptors employed such as tungsten, niobium, tantalum and carbon. It was concluded that catalytic action of the susceptor material was involved in the etching process.

2.0 Amorphous Semiconductor Materials

Personnel: H. C. Gatos, A. F. Witt; N. Platakis
Sponsorship: National Aeronautics and Space Administration

A method has been developed for the preparation of vitreous materials which essentially overcomes some of the main problems associated with the characterization and study of such materials. These problems are chemical homogeneity, porosity and lack of well-defined geometrical shapes. The salient steps of the new method are as follows: the constituents of the vitreous system are placed in the desired proportions in a quartz ampule which is evacuated and sealed off. Then the ampule is fitted to a horizontal shaft of a motor. The shaft-ampule arrangement can be placed in and out of a horizontal furnace while the ampule is being rotated at about 25 rpm. After the material is molten the ampule is withdrawn from the furnace and while still under rotation is quenched either in air or other media. The resulting hollow cylinders are (chemically) extremely homogeneous, exhibit higher strength than if prepared by other methods and are suitable for electrical and optical characterization. The method has been extensively applied on the system As_2Se_3-Sb_2Se_3. The overall reproducibility of the method was found to be excellent.

The glass formation region of the system As_2Se_3-Sb_2Se_3 and the vitreous-crystalline transformation were investigated in some detail. Electrical and optical properties of both the vitreous and the crystalline state were studied as a function of composition. For a given composition the activation energy of the vitreous state

was greater than in the crystalline state by 0.2 to 0.4 eV. The activation energies ranged from 1.85 for pure As_2Se_3 to 1.2 eV for pure Sb_2Se_3. An excellent agreement was found between the values obtained from infrared and electrical resistivity measurements. Work on this system is being continued.

3.0 Semiconductor Thin Films

Personnel: H. C. Gatos, A. F. Witt; M. Lichtensteiger, I. Lagnado, A. Vejux, B. Wessels, J. M. Harris

Sponsorship: Advanced Research Projects Agency and I.B.M. Fellowship

Research on semiconductor thin films is being pursued along three experimental approaches, sputtering, direct evaporation and vapor transport.

An RF-sputtering unit has been employed in a diode configuration for the preparation of cadmium sulfide films up to 5 microns thick on amorphous as well as on crystalline substrates. X-ray diffractometer tracings showed exclusively (000ℓ)-peaks with ℓ = 2, 4, 6 ... indicating a highly preferred basal plane orientation parallel to the substrate. Electron diffraction patterns indicate essentially the same structural features as those obtained from single crystal cadmium sulfide. It is significant to point out that in connection with this work p-type conduction in (000ℓ) oriented cadmium sulfide films was obtained by chemical means for the first time. Phosphane was used in the presence of the argon atmosphere during sputtering. DC Hall measurements showed that the p nature of the prepared films was maintained from the liquid nitrogen temperature to 170°C. By sputtering p-type cadmium sulfide on n-type cadmium sulfide substrate p-n junctions were achieved.

Cadmium sulfide films were also prepared by direct evaporation on glass substrates. Deposition was carried out at temperatures ranging from 20°C to 400°C. X-ray diffraction techniques showed here again that preferred orientation is obtained along the c-axis. A liquid nitrogen cooled substrate stage has been designed aimed at condensing entirely the vapor phase in the substrate region. Composition analysis of the deposit should give the ratio of the vapor species for various experimental conditions. Control of the composition is expected to be obtained through reflectors near the substrate surface. Controlling the stoichiometry of cadmium sulfide or other similar compounds is a problem of fundamental importance.

Silicon carbide films were prepared by vapor transport employing silane and propane in a hydrogen atmosphere. The deposition of the silicon carbide films took place at temperatures ranging from 1500-1600°C. The growth characteristics are best described by a model in which the surface of the samples is in equilibrium with the reactants diffusing through a boundary layer. The deposition progress is inhibited above 1650°C by the increasing thermal etching rate and the amount of the reactants which can diffuse to the sample surface. Electrical characterization of undoped hexagonal (alpha) silicon carbide layers grown on p-type alpha silicon carbide substrates indicate that the resistivity and Hall mobility of the grown layers were approximately 0.40 ohm-cm and 200 cm^2/V-sec, respectively at 77°K.

4.0 Superconductors

Personnel: H. C. Gatos; J.T.A. Pollock, P. Bellin

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

The detailed study of the superconducting properties of ternary Nb-Ti-V alloys has been completed; however, some unusual effect of neutron irradiation on some of these alloys in the cold-rolled conditions were observed. Several of these alloys were irradiated in a fast neutron flux of 3.7×10^{19} neutron per cm^2 in the swimming pool reactor of Union Carbide Corporation's Sterling Forest Reactor. During irradiation the temperature of the samples was maintained below 70°C. Superconducting transition temperature, T_c and critical current J_c, data were obtained at 4.2°K. Both T_c and J_c were found to degrade as a result of irradiation. This unexpected behavior has been attributed to a "shorting" in the flux motion paths due to defect overlap. This type of the model has been found to explain some earlier observations on cold-rolled alloys of refractory superconducting materials in other laboratories. On the other hand, niobium nitride samples irradiated under similar conditions exhibited an improved current carrying capacity. In this case it appears that neutron-induced defects act as pinning centers for fluxons.

5.0 Semiconductor Growth and Characterization

Personnel: H. C. Gatos, A. F. Witt; M. Lichtensteiger, G. Galyon, J. Sandor, R. Singh and D. Miller

Sponsorship: Advanced Research Projects Agency, National Science Foundation and General Telephone and Electronics Fellowship

The Electronic Materials Group has continued its efforts towards the growth of single crystals from the melt and the vapor phase. In addition, extensive effort has been made to characterize semiconductor single crystals by electrical, chemical and optical techniques with regard to crystalline perfection and impurity homogeneity. Significant progress has been made in achieving crystalline films of cadmium sulfide by sputtering, indium antimonide single crystals of extreme homogeneity, germanium single crystals with controlled variations of impurity distribution and single crystals in the gallium antimonide-indium antimonide system. Before the results on the characteristics of the various single crystal systems are outlined it should be noted that the Czochralski type puller designed and constructed by the Electronics Materials Group has been refined to the point where crystal growth parameters such as gradients in the solid-liquid interface can be controlled during the growth of both indium antimonide and germanium crystals. A Peltier effect arrangement has been incorporated into the puller so that the microscopic rate of growth can now be monitored during the entire growth process.

Single crystals of GaSb-InSb alloy have been grown by the Czochralski method and samples cut from the crystals have been, and are being, characterized optically and electrically. The maximum InSb content of the crystals is about 20 wt. percent. As the InSb content increases beyond 8 wt. percent there is an increasingly severe problem with cracking. However, samples large enough for testing may be cut from the uncracked regions which are primarily to be found in the core region, as opposed to the off core region. Electrical measurements show that the ionization potential of the acceptor sites (all crystals grown were p-type) decreased with increasing InSb, from .024 eV for GaSb to .010 eV at 8 wt. percent GaSb. From 8-20 wt. percent InSb the ionization potential remains constant at .01 eV. The value of the band gap as determined by

the Hall measurements varies from .82 eV for GaSb to .46 eV for 20 wt. percent InSb. High temperature Hall measurements (up to 600°C) are now in progress to assess certain band structure aspects.

The electrical characteristics of microheterogeneities are being studied in germanium single crystals, as a function of thermal asymmetry during growth. Using interference contrast microscopy and the etching technique previously developed for revealing impurity heterogeneities in gallium-doped germanium, it is possible to relate electrical properties directly to the microdistribution of impurities. We have successfully grown single crystals of constant diameter by the Czochralski method which include at least five regions of varying impurity homogeneity. The associated electrical property differences are currently being examined. Profiles of Hall mobility measurements made from room temperature down to liquid nitrogen temperature indicate that the effect of lattice scattering on carrier mobility does not vary from region to region, while ionized impurity scattering does lead to mobility differences that increase with decreasing temperature. Preliminary results indicate that for a given impurity concentration there may be more than a 10% enhancement of carrier mobility in highly homogeneous unstriated material as compared with striated material. Furthermore, the core material shows a slight increase (4-5%) in mobility over the off-core materials. Samples cut perpendicular to the <111> crystal axis further reveal a decreased mobility (8-10%) as compared with samples cut parallel to the <111> crystal axis. This behavior is being explored further, and being simultaneously compared directly with evidence obtained by interference contrast microscopy from etched material immediately adjacent to the samples used for eleccrical measurement. In this way a complete record will be obtained of the configuration of impurity striations within each crystal characterized.

Single crystals of Ge heavily doped with Ga were grown by the Czochralski techniques in the <111> direction. The impurity level was maintained in such a way that during growth the system was on the verge of instability due to constitutional supercooling. Rotation rates from 15-70 rpm and pulling rates from 1.5 cm/hr to 5 cm/hr were used. At moderate crystal growth rates (i.e. 2.5-3.5 cm/hr) perturbations in the growth interface in the form of sinusoidal oscillations could be revealed by etching. The wave length associated with these oscillations ranges from 30-60 μ in the radial direction

and considerably higher in the circumferential direction. A phase velocity ranging from 5-15μ/sec was determined. The core part of the interface can be stable under conditions that lead to instability in the"off-core" region. The most critical location for the initiation of the oscillations at the growth interface is the region between the "core" and "off-core". The oscillations then propagate away from the core as waves. Striations associated with the oscillating interface around the core parallel to the growth direction are seen as concentric rings around the core. The causes of instability and its relationship to the thermal fluctuations, the fluid flow and associated mass and momentum boundary layers are being theoretically analyzed.

The depth of abrasion induced surface damage on the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of indium antimonide single crystals has been successfully measured using x-ray anomalous transmission. Integrated intensities were measured from all six [220] planes perpendicular to the (111) and $(\bar{1}\bar{1}\bar{1})$ planes in the damaged slices. Differences in adsorption were related to the depth of damage. The results show that for a given cold work the depth of damage is greater on the B than on the A surfaces. The linear effective absorption coefficient for the dislocation-free indium antimonide specimen used has determined to be 10.01 cm^{-1} for AgK_{α} radiation. Using both anomalous transmission topography and integrated intensity measurements, the growth characteristics of Czochralski-grown indium antimonide crystals doped with tellurium have been studied. Misalignment in both "core" and "off-core" regions of up to three minutes of arc have been measured and preliminary work indicates that the strain is of a twisting nature. The sense and magnitude of the strain configurations are being related to growth mode and doping and also tc fundamental aspects of the atomic mechanisms of crystal growth.

6.0 Decomposition of Silver (II) Oxide

Personnel: A. F. Witt; O. Sandven

Sponsorship: National Aeronautics and Space Administration

In air, AgO decomposes slowly to Ag_2O in the temperature range 111°C-133°C. The decomposition curve is sigmoid and in good agreement with published results. Samples with small particle size, or in compacted form decompose faster than loose powder. The activation energy is approximately 30 Kcal/mol. No change in the activation energy was observed in vacuum although the reaction rate is much higher than in air and no longer sigmoid.

In air, the electrical resistance R of cold pressed samples of AgO increases initially with time t according to:

$$\log R/R_o = K_1 t$$

where K_1 is a constant and R the initial resistance. After a relatively short time, the slope changes abruptly and the resistance follows the relationship:

$$\log R/R_o = K_2 t + a$$

In vacuum, this change in slope does not occur, and the rate is again higher.

In the temperature range 18°-70°C (in air), the resistance varies reversibly according to:

$$\log R = C + K\ 1/T$$

An apparent activation energy for conduction of about 0.50 eV was determined. Infrared adsorbtion experiments failed to reveal an energy gap in this range. It may thus be assumed that the change in resistance with temperature is more likely due to the heat of adsorbtion of ambient gases than due to an actual gap.

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XI. SUPERCONDUCTIVE MATERIALS

(Personnel from Department of Metallurgy and Materials Science except where indicated)

Faculty:

R. M. Rose, Associate Professor
L. W. Gruenberg, Associate Professor, Electrical Engineering
J. Wulff, Professor Emeritus and Senior Lecturer
J. W. Hafstrom, Assistant Professor
M. L. A. MacVicar, Instructor, Physics

Graduate Students:

D. C. Hill, Teaching Assistant
J. G. Kohr, Teaching Assistant
D. D. Morrison, Allegheny Ludlum Fellow
S. Ochiai, Research Assistant
J. R. Pearson, Research Assistant
R. L. Ricketts, Teaching Assistant
W. R. Stowell, Teaching Assistant
L. Weinman, Teaching Assistant

Support Staff:

S. Zayac, Student Assistant
I. M. Puffer, Engineering Assistant
Phyllis M. Stratton, Secretary

Personnel who have left:

J. R. Pearson (to INCO Research Laboratory, Sterling Forest, N. Y.)
R. L. Ricketts (to General Electric Knolls Atomic Power Laboratory, Schenectady, N. Y.)

Degrees Granted:

R. L. Ricketts, Ph. D., Metallurgy, June 1969
J. R. Pearson, Ph. D., Metallurgy, June 1969
J. W. Hafstrom, Ph. D., Metallurgy, September 1969
D. C. Hill, S. M., Metallurgy, September 1969
G. C. Ferriss, S. B., Metallurgy, September 1969

Sponsorship:

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Office of Naval Research, Nonr 3963-16, DSR 74611

Research Report:

1.0 High-Field Solid Solution Superconductivity

1.1 Structure and High Field Properties of Quaternary Nb-Ti Base Alloys

The aging behavior of a niobium-titanium alloy containing 60 weight per cent titanium and small additions of oxygen and erbium or scandium was characterized and related to superconducting properties. The ternary and quaternary alloys were melted in an argon-arc furnace, cold reduced to 10 mil wire and 15 mil foil, and aged for various times at temperatures between 250°C and 1000°C. Omega and alpha phase transformations and oxide precipitation processes were followed by lattice parameter, resistivity, critical magnetic field, and critical current density measurements, as well as by X-ray diffraction intensity and metallographic investigation. The optimum one-hour aging temperatures for producing omega and alpha phase precipitation were found to be 400°C and 500°C respectively. Aging at 1000°C produced only oxide precipitation. It was found that oxygen and rare earths stabilize the alpha phase but have little effect on omega precipitation.

In determining the fluxoid pinning effectiveness of a given second phase precipitate both the inherent pinning strength (F_p) and the number density (N_p) of the precipitate particles were considered. The most effective fluxoid pinning precipitate in these alloys was found to be the omega phase which precipitates on a fine scale producing an extremely high number density of pinning sites. Critical current density data were plotted on J_cH versus H graphs, and it was demonstrated that the dominant fluxoid pinning precipitate in superconducting samples can be identified from the shape of these curves.

2.0 Superconductivity in the Transition Metals

2.1 The Critical Field of Nb

The transverse and longitudinal resistive critical fields of Nb wires with drawing strains up to 11 were measured. The magnitude and anisotropy of the resistive crystal field were both much greater than the bulk Ginzburg-Landau parameters indicate, even if "internal surface" nucleation of superconductivity is assumed. We have suggested, using simple calculations, that these effects are due to superconductivity in the dislocation cell walls created by drawing or swaging. We have worked out a simple model for this effect and tested the model successfully by various experiments. Experiments indicate a very remarkable H_c-T curve for this material, and large transition-width changes on recovery.

2.2 Grain Size Control in Nb

Preliminary experiments indicate that grain growth can be intentionally severely inhibited by oxygen clusters.

2.3 Theoretical Calculations on Defects in the Fluxon Lattice

Computer-aided variational calculations were made to examine the stability of various lattice defects in the flux line lattice which exist in the mixed state of Type II superconductors. The stable configurations agreed with the direct experimental observations of Essmann and Träuble, if the dislocations and vacancies were assumed to be associated with pinning centers. The presence of pinning centers can also explain the frequencies with which the various defects are observed. The Peierls potential for dislocations was also calculated, as well as the theoretical shear stress for the perfect lattice.

2.4 Surface Nucleation: Structural Effects

Recent work in the literature shows that surface abrasion leads to the persistence of superconductivity at magnetic fields much higher than the bulk critical field. We were able to do critical experiments showing that such effects are due to severe structural effects (from the abrasion) and not, as is currently accepted, to changes in the boundary conditions for sheath nucleation.

2.5 Controlled Pinning by Surface Relief in Pb-Ti Alloy Foils

We have separated the three main contributions to J_c in Pb-Ti foils experimentally. We are now in a position to selectively introduce pinning centers of known strength, geometry and density, and confirm that we have done this by direct observation. Thus, for the first time, we may be able to do truly quantitative experiments on fluxon pinning.

3.0 Tunneling

3.1 Nb Single Crystals

Our measurements at 0.48°K and above on high-purity Nb crystals have revealed direct evidence for the existence of a second gap for superconductivity, at crystal orientations where such a gap would be predicted by the band structure of Nb and currently accepted multiband theory. The second gap is 1/10 the size of the first and is independent of temperature over the range of our measurements (0.48 to 4.2°K).

3.2 Re Single Crystals

Because Re is an HCP metal and presumably quite anisotropic, and is also in Group VII (in the periodic table) in the transition series, we have initiated work on the growth and tunneling into Re single crystals. Together with our results for Nb, we hope the data for Re will clarify our picture of transition metal superconductivity.

3.3 "Synthetic" Tunneling Barriers

Work has begun on the properties of amorphous C and Ge barriers, which will be used as a check on the Nb and Re tunneling work (which uses oxide barriers), as a barrier on alloys, and also because such barriers may be useful practically, e.g. in the creation of stable Josephson junctions.

4.0 Superconducting Composites

We are presently examining the AC response of superconductors in the power-audio and VHF frequency domains, as in both cases practical utilization can be greatly accelerated if the materials problems can be solved.

5.0 High T_c and Structure

In our investigation of the structure and properties of granular high-T_c films, we have found direct evidence of structural instability in the edges of Al and Al-.3% Mg films, confirming directly the "phonon-softening" school of thought on T_c enhancement.

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J. R. Pearson and R. M. Rose, "The Resistive Critical Field of Niobium Wires", to appear in App. Phys. Letters.

Submitted:

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D. C. Hill, J. G. Kohr, and R. M. Rose, "On Surface Nucleation of Superconductivity at Abraded Surfaces", to Phys. Rev. Letters.

XII. CERAMICS

(All Personnel from Department of Metallurgy and Materials Science.)

Faculty:

R. L. Coble, Professor
W. D. Kingery, Professor
C. J. Mogab, Assistant Professor
D. R. Uhlmann, Associate Professor
B. J. Wuensch, Associate Professor

Graduate Students:

H. T. Anderson, Teaching Assistant
R. G. Block, Research Assistant
J. R. Booth, Research Assistant
H. K. Bowen, Graduate Fellow
P. Chabrier, Research Assistant
S. A. Cho, Research Assistant
J. A. Conwicke, Research Assistant
P. N. Dangel, Research Assistant
R. Gentilman, Research Assistant
C. A. Goodwin, Research Assistant
T. R. Guillermo, Research Assistant
J. K. Jenkins, Research Assistant
R. N. Katz, Graduate Student
K. S. Kim, Research Assistant
K. Kitazawa, Research Assistant
I. Kohatsu, Graduate Fellow
W. T. Laughlin, Research Assistant
J. H. Li, Research Assistant
A. M. Mocellin, Research Assistant
H. J. Modetz, Research Assistant
R. L. Pober, Research Assistant
J. J. Rasmussen, Research Assistant
W. L. Robbins, Research Assistant
S. C. Samanta, Research Assistant
J. Sauvage, Research Assistant
C. Seaton, Research Assistant

R. N. Singh, Research Assistant

R. J. Tiernan, Research Assistant

Support Staff:

D. M. Fellows, Technician

A. E. Freker, Technician

P. A. Kearney, Technician

R. L. Stanton, Technician

F. D. Wilson, Technician

Antoinette Centorino, Secretary

Susan Mogab, Secretary

Personnel Who Have Left:

R. G. Block (Now at Wright-Patterson Air Force Base, Ohio)

S. A. Cho (Now at RCA, Moorestown, New Jersey)

J. A. Conwicke (Now at DuPont Company, Wilmington, Delaware)

R. N. Katz (Now at AMMRC, Watertown, Massachusetts)

W. T. Laughlin (Now at Kirtland Air Force Base, New Mexico)

J. Li (Now at American Research Instruments, Arlington, Massachusetts)

J. J. Rasmussen (Now at Battelle-Northwest Labs, Richland, Washington)

R. J. Tiernan (Now at Raytheon, Waltham, Massachusetts)

P. J. Vergano (Now at Owens-Illinois Glass Company, Toledo, Ohio)

Degrees Granted:

H. T. Anderson, S.M., Ceramics, September 1969

R. G. Block, S.M., Ceramics, September 1969

S. A. Cho, Sc.D., Ceramics, September 1969

J. A. Conwicke, Sc.D., Ceramics, January 1969

P. N. Dangel, Ph.D., Ceramics, September 1969

R. N. Katz, Sc.D., Ceramics, September 1969

W. T. Laughlin, Sc.D., Ceramics, January 1969

J. H. Li, Sc.D., Ceramics, January 1969

J. J. Rasmussen, Ph.D., Ceramics, January 1969

R. J. Tiernan, Ph.D., Ceramics, January 1969

P. J. Vergano, Sc.D., Ceramics, June 1969

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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, (3) research on the structure and properties of noncrystalline solids, and (4) materials synthesis and preparation. Each of these areas of research is described in detail in the report.

1.0 Kinetics of Phase Changes, Diffusion, and Microstructure Development

1.1 Grain Boundary Diffusion Studies (AEC)

Personnel: B. J. Wuensch; R. J. Tiernan

A study of the diffusion of Tl in single-crystal, bicrystal and polycrystalline KCl has been completed. The system was chosen for study because Tl is a highly polarizable ion for which transport should be greatly influenced by the presence of grain boundaries. Diffusion of Tl in single-crystal KCl was found to be extrinsic in the temperature range 230°-480°C and describable in terms of an activation energy of 0.25 eV and a pre-exponential term, D_o, of 9×10^{-11} cm^2/sec. Diffusion in the temperature range 480-727°C was intrinsic and characterized by an activation energy of 1.42 eV and D_o of 6×10^{-3} cm^2/sec. These results provide 2.34 eV as the activation energy for Schottky defect formation, a value in good agreement with estimates of other work.

Grain boundary diffusion was studied in the temperature range 550-865°C, a region in which the single crystal measurements indicate that bulk diffusion is intrinsic. Enhanced diffusion along grain boundaries was observed in some, but not all samples. Typical values of the product of grain boundary width and diffusion coefficient were small (1 to 20×10^{-14} cm^3/sec). The grain boundary effect was not reproducible and is attributed to small amounts of impurity. Water vapor, if present during the fabrication of bicrystals, was shown to cause a marked increase in boundary diffusion.

1.2 Ion Transport in Crystals (AEC)

Personnel: B. J. Wuensch; K. S. Kim

Studies of the relation between transport properties and structure are continuing. Cation diffusion in oxides of the hexagonal wurtzite type is being examined for possible anisotropy. Such measurements provide insight into the nature of the path followed by the migrating ion. Measurement of self-diffusion rates for Zn^{65} in single-crystal ZnO as a function of temperature and crystallographic direction have begun, and a few preliminary diffusion coefficients have been obtained.

1.3 Diffusion Mobility Structure in Single Crystal Alumina (AEC)

Personnel: R. L. Coble; W. L. Robbins

Diffusion coefficients and mobilities have been determined in Ti-doped alumina single crystals by the observation of the migration of color boundaries.

When Ti-doped samples are fired in a reducing atmosphere, a pink crystal is obtained, and when fired in an oxidizing atmosphere a clear crystal results. This clearing takes place due to diffusion of some defect or defects which cause a change in the effective oxidizing or reducing atmosphere surrounding the transition metal dopant. By firing the reduced crystals in an oxidizing atmosphere under the influence of a D-C field, the diffusion coefficient can be determined by measurements perpendicular to the field and mobilities can be determined by measurements parallel to the field; application of the Nernst-Einstein relationship gives the charge on the diffusing species.

By combining the diffusion studies with precise density determination, it is anticipated that the defect structure of alumina can be better understood.

Further studies will be extended to Co and/or Ni-doped samples where the valence change is of a two-three type. In addition to oxidation studies, reduction studies will be performed.

1.4 Effect of Pressure on Grain Boundary Self-Diffusion (AEC)

Personnel: R. L. Coble; R. Pober

A literature survey has yielded data on the effect of pressure on lattice diffusion and also has shown a few solutions to the grain boundary diffusion problem. From the indicated values of lattice diffusion in lead and values for the grain boundary diffusion at one atmosphere, it is now possible to select experimental conditions which will yield reliable results from which to calculate grain boundary diffusion coefficients as a function of pressure.

Isotope counting equipment has been set up to count the Pb^{210} gamma decay. This will eliminate the problems sometimes encountered when measuring the beta decay of the Bi^{210} daughter. Diffusion of the radioisotope will be done in an externally heated "bomb" in a silicone oil, temperature-controlled bath.

Initial experiments will be directed toward determining whether the activation volume is positive or negative for grain boundary self-diffusion in lead.

1.5 Crystallization and Melting Kinetics of Germanium Dioxide (AEC)

Personnel: D. R. Uhlmann; P. J. Vergano

The effects of melting temperature and atmosphere upon the state of reduction of germanium dioxide glass have been determined, and glasses varying from very nearly stoichiometric to .004% reduced have been prepared. Growth rates of hexagonal germanium dioxide crystals were measured in four glasses of differing stoichiometries over a range of undercoolings from 3 to 416°C. In air, nitrogen, and oxygen atmospheres, the crystal thickness was found to increase linearly with time at all temperatures studied. The measured crystal growth rates covered a range from 10^{-8} cms/sec at 416° undercooling to a peak of 10^{-5} cms/sec at about 75° undercooling. Crystal growth rates in all the glasses exhibited the form of growth rate variation with temperature typical of glass forming materials. Crystal growth rates were found to increase with the state of reduction of the glass over the full temperature range studied. Growth rates in the .004% reduced glass were a factor of 2 greater than those in stoichiometric glass at high undercoolings and up to a factor of about 4 greater at low undercoolings.

Various extrinsic growth effects were observed. A form of rapid growth independent of specimen geometry occurring at temperatures above 950°C and a geometry-dependent type of extrinsic growth occurring at lower temperatures were both associated with sodium impurities. Extrinsic

growth rates estimated to be two or three orders of magnitude greater than intrinsic growth rates were observed.

Using viscosity data of other investigators obtained on glasses melted in the same way as one of the glasses studied, it was determined that the reduced growth rate

$$\frac{\text{growth rate x viscosity}}{1 - \exp^{-\left(\frac{\Delta H_F \Delta T}{RTT_E}\right)}}$$

of GeO_2, a low entropy of fusion material, is independent of undercooling over the full range of undercooling studied, 16 to 416°C.

Melting rates were measured using a slightly reduced glass (.002% reduced) and a very nearly stoichiometric glass over a temperature range from 5° to 23° superheat. The reduced glass exhibited faster melting in this temperature range. A plot of the growth and melting rates at temperatures near the melting temperature against temperature was found to be continuous with no change in slope through the melting temperature for both glasses whose melting rates were measured.

Melting and crystallization specimens always exhibited nonfaceted crystal-liquid interfaces. Consistent with this, an x-ray analysis of growth specimens indicated that growth was relatively isotropic. The nonfaceted interface morphologies, the growth isotropy, the reduced growth rate independent of temperature, and the growth-melting rate continuity at the melting temperature all lend support to reasoning based on the Jackson model of the crystal-liquid interface.

1.6 Effects of High Pressure on Transformation Kinetics (AEC)

Personnel: D. R. Uhlmann

The effects of high pressure on the kinetics of crystallization and melting, as well as upon the kinetics of solid-solid transformations are being investigated. The materials being studied in the crystallization and melting study include SiO_2 and B_2O_3, while the solid-solid transformation is $CaCO_3 + SiO_2$.

1.7 Investigation of Forming Sintered $BaTiO_3$, $SrTiO_3$, and $MgTiO_3$ (AEC)

Personnel: W. D. Kingery; P. Chabrier

An investigation is underway to obtain sintered $BaTiO_3$, $SrTiO_3$, and

$MgTiO_3$ starting from powders prepared by freeze-drying. The necessary conditions are fine and uniform particle size, uniform grain density, grain growth inhibition which is attempted by using such additives as Sm_2O_3, Ca_2O_3, Al_2O_3, La_2O_3, Nb_2O_5, and Ta_2O_5 and a diffusible atmosphere of oxygen.

2.0 Relationship of Properties to Composition, Crystal Structure and Microstructure

2.1 Crystal Structure Studies (AEC)

2.1.1 Crystal Chemistry of Glass-Forming Sulfides

Personnel: 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. A determination of the crystal structure of this phase has been completed using crystals synthesized from As_3SbS_6 glass under 1000 bars pressure. The structure is composed of thick (9.1 Å) slabs. Both arsenic and antimony have the customary trigonal-pyramidal coordination of sulfur. The basic unit of the structure is an eight-membered ring, consisting of alternating pairs of Sb and As pyramids. All rings are oriented normal to the slab. Within a slab the rings are linked in a meandering, very open "glass-like" network. The structure bears no relationship to that of either Sb_2S_3 or As_2S_3.

Attempts are being made to synthesize single crystals of As_2S_3. This structure is only roughly known, and a refinement of the atomic positions seems desirable. Crystals of As_2Se_3 have been successfully prepared. Preliminary results indicate that this phase is isostructural with As_2S_3.

2.1.2 Cation Distribution in Nonstoichiometric Spinels

Personnel: B. J. Wuensch; H. T. Anderson

An intermediate spinel phase XZ_2O_4 occurs in a number of ceramic systems. The stability field of the phase commonly extends over wide ranges of stoichiometry toward Z_2O_3 at elevated temperatures. Magnesium

gallate spinels have been synthesized by freeze-drying techniques with compositions extending over the complete range of homogeneity at 1400°C. Precision lattice constant measurements combined with density determinations revealed that excess Ga^{3+} is incorporated into the structure by the replacement of 3 Mg^{2+} by 2 Ga^{3+} and a vacancy. It has been shown that at 1400°C 84.7% of the occupied tetrahedral sites in stoichiometric $MgGa_2O_4$ contain Ga^{3+} and 59.1% of the octahedral sites are occupied by Ga^{3+}. The electron content of each type of site has been refined for nonstoichiometric compositions as well. The number of electrons contained in the tetrahedral site was found to increase as the departure from stoichiometry increased. This indicated that the excess Ga^{3+} has a marked preference for the tetrahedral site. It is not possible to determine the atomic occupancy of each type of site solely on the basis of composition and electron content, since the distribution of vacancies among the sites is unknown. We plan to resolve this question by a two-step refinement of site occupancies. The number of electrons contained in each type of site will be refined subject to the constraint that the total number of electrons correspond to that given by the composition of the phase. The atomic content of each site will then be refined subject to the constraints of composition and the electron content previously determined.

2.1.3 Structural Study of the Phase Transformation in CuAgS

Personnel: B. J. Wuensch; T. R. Guillermo

CuAgS exhibits a phase transformation from an orthorhombic to a hexagonal structure at a temperature in the neighborhood of 100°C. The transformation involves an unusually large amount of energy. In an analogous transformation in Cu_2S both Cu diffusion rates and conductivity increase by several orders of magnitude. High temperature x-ray diffraction is being employed to determine the crystal structures of both phases of CuAgS at several temperatures spanning the transformation point. The resulting structural data will be used to study thermal vibrations of the atoms near the transformation point and to correlate thermal expansion with structural change. A heating device has been constructed for a single crystal diffractometer. The necessary sample-mounting techniques have been developed, and collection of the diffraction data is proceeding.

2.1.4 Analysis of Superstructures

Personnel: B. J. Wuensch

Analysis of the structures of several superstructures is continuing. It is hoped that details of these structures will provide the reasons for the perturbations of a simpler structure which leads to the increased size of the lattice. Many Pb-containing sulfides are closely related to a simpler rock salt-like array of atoms. $PbAgSbS_3$ is a severely distorted derivative of the rock salt structure with an ordered arrangement of metal atoms. While the study is not yet complete, it appears that its phase is isostructural with its arsenic analogue. Another superstructure, $Pb_{13}As_7S_{13}$, has been found to be based on sizable slabs of rock salt structure rotated relative to one another. Also under continuing study is Fe_7S_8, a superstructure formed by vacancy ordering in a nonstoichiometric structure of the NiAs type.

2.2 Crystal Chemistry of Sulfosalts (NSF)

Sulfosalts are minerals in which one or more metal atoms are combined with a Group V metal and sulfur. The crystal chemistry of these materials is extremely complex. Because of formidable experimental problems associated with their study, very few structures are known.

2.2.1 Bismuth Sulfosalts

Personnel: B. J. Wuensch; J. K. Jenkins, I. Kohatsu

The primary tool for distinguishing Pb and Bi (which have nearly identical scattering powers for x-rays) in a structure is a slight difference in metal-sulfur bond lengths. Only one Bi sulfosalt has been carefully refined. The structure of emplectite, $CuBiS_2$, has therefore been refined to obtain a precise measure of Bi coordination. The structure consists of parallel chains of CuS_4 tetrahedra and a double chain of BiS_4 square pyramids. The shortest Bi-S separation was found to be 2.53 Å. In contrast, Pb-S separations have never been found to be less than 2.73 Å. A determination of the structure of aikinite, $PbCuBiS_3$, has been completed. The rough details of this structure were known, but the S positions were uncertain and Pb and Bi were not distinguished. The structure is an interesting derivative of the Bi_2S_3 structure. Pb sub-

stitutes for 1/2 of the Bi in the latter structure and Cu is located in a normally unoccupied interstice. Also under investigation is the structure of gladite, $CuPbBi_5S_9$, which appears to be a superstructure based upon $PbCuBiS_3$ and in which only a portion of the tetrahedral interstices are filled by Cu. Further work is concerned with a newly discovered phase of composition $Pb_{10}Cu_4Bi_{10}S_{27}$. This structure bears no obvious relation to Bi_2S_3 but yet has one lattice constant characteristic of the bismuth chains present in $PbCuBiS_3$ and $CuBiS_2$.

2.2.2 Antimony Sulfosalts

Personnel: B. J. Wuensch; S. A. Cho and J. K. Jenkins

The system $PbS-Sb_2S_3$ contains at least 19 intermediate phases. None of their crystal structures are known. Curiously, there is virtually no correspondence with the sequence of phases occurring in the system $PbS-As_2S_3$. Of particular interest is the plagionite group, an apparent homologous series $Pb_{3+2n}Sb_8S_{15+2n}$ (n = 0 to 3) in which two lattice constants remain invariant, while the third increases with n. A determination of the crystal structure of plagionite, $Pb_5Sb_8S_{17}$, has been completed. The structure contains a cluster of Pb octahedra sharing edges. These clusters are flanked by a sheet of Sb square pyramids. The two types of polyhedra together form a twisted ribbon of PbS-like structure. The composition and properties of the plagionite group may be explained in terms of a gradual increase in length (i.e., the "pitch" of the twist) of the PbS-like region of the structure in successive members of the series. A structure determination of semseyite, $Pb_9Sb_8S_{21}$, is in progress to confirm this proposal.

2.3 Grain Boundaries, Impurities and Pores in Al_2O_3 (AEC)

Personnel: W. D. Kingery; A. Mocellin

Sintered aluminum oxide, of high purity and controlled dopant concentration has been prepared. The influence of magnesium as a dopant and the heat-treating atmosphere on the time and temperature dependence of grain growth has been investigated.

The possibility of boundary diffusion controlled creep has been investigated and the results indicate that in the temperature range 1600°-1900°C under ∿1000 psi compressive stress, the deformation behavior of

large grain size samples (∿60 microns) is not in contradiction with Coble's mechanisms.

2.4 Dislocations Behavior in Alkaline Earth Fluorides (AEC)

Personnel: R. L. Coble; R. N. Katz

The behavior of dislocations in pure calcium fluoride, barium fluoride and strontium fluoride, as well as calcium fluoride doped with various amounts of neodymium was studied. The stress-velocity relationships for both edge and screw dislocations in single crystals of calcium fluoride and for edge dislocations only in barium fluoride were investigated utilizing a modified Gilman and Johnston technique. Analyzing the data in terms of power function, $v = A\tau^m$, it was found that the alkaline earth fluorides have a lower stress-velocity exponents, m, than do other ionic crystals. Direct evidence that a fraction of the screw dislocations in pure calcium fluoride and barium fluoride possess greater mobility than edge dislocations was obtained. Doping calcium fluoride with as little as 70 ppm Nd^{3+} eliminated the fast screw dislocations. The mobility of screw dislocations in calcium fluoride was rationalized on the basis of a Fleisher "rapid solution hardening" model. The phenomenon of trails associated with screw dislocations in the alkaline earth fluorides was also investigated.

The behavior of edge dislocations in calcium fluoride crystals of various purity, indicated that a change in principal drag mechanism, from an extrinsic to intrinsic drag occurs with increasing stress. It is hypothesized that the extrinsic drag mechanism for Nd^{3+} doped calcium fluoride is the reorientation of $Nd^{3+} - F^-$ dipoles in the stress field of the moving dislocation.

Stress-strain curves for pure calcium fluoride, barium fluoride and calcium fluoride doped with neodymium were obtained for compression along the $[11\bar{2}]$. Neodymium was found to influence the yield stress but not the work hardening rate of calcium fluoride.

2.5 Dislocation Behavior in Fluorite Structure Materials: UO_2 and ThO_2 (AEC)

Personnel: R. L. Coble; R. N. Singh

To elucidate whether other fluorite structure materials, namely, uranium oxide and thorium oxide, show behavior similar to that observed in the alkaline earth halides, single crystals of UO_2 and ThO_2 will be deformed

and stress-velocity data will be obtained for varying temperature, stoichiometry and impurity contents. It is hoped that analysis data for dislocation motion and activation volumes will permit the elucidation of the drag mechanism controlling the dynamics of dislocations in these materials. Moreover, the effect of the above-mentioned variables on yielding behavior will also be studied and related to the basis of dynamic dislocation behavior.

2.6 Thermophysical Properties of Nonstoichiometric Materials in a Thermal Gradient (AEC)

Personnel: W. D. Kingery; H. K. Bowen

Thermal gradient studies are to be made on single crystal and polycrystalline samples of wustite ($Fe_{1-x}O$). Measurement of structure-sensitive properties will then allow empirical determination of composition variation and property changes resulting from the thermal gradient. Measurement of mass transport will allow calculation of the Soret coefficient and chemical diffusion coefficient.

Single crystals of wustite have been grown by chemical vapor deposition. Facilities have been completed for static growth, including a fused quartz encapsulation system and gradient furnaces with precise long-term temperature control. In addition to the growth of wustite, single crystals of Fe_3O_4, Fe_2O_3, NiO, CoO, $Ni_xMg_{1-x}O$, and MgO have been grown.

A functional oxygen pump employing calcia-stabilized zirconia is under development to control and measure the oxygen potential during powder preparation and property measurements.

3.0 Structure and Properties of Noncrystalline Solids

3.1 Evaporated Amorphous Silicon Thin Films (AEC)

Personnel: C. J. Mogab and W. D. Kingery; J. Sauvage

Thin films of silicon deposited on sapphire substrates by electron beam evaporation at room temperature, 10^{-7} torr, and 15 Å/sec are monitored in "situ" by conductivity measurements at annealing temperatures from 100°C to 400°C. Steady-state annealing temperature is obtained in less than 30 seconds and controlled better than 5°C during four decades of time in logarithm scale. A quartz lamp included in the vacuum system and a three modes controller are responsible for such heating characteristics.

The irreversible decrease in conductivity at constant annealing temperature is found to show discrepancies from a straight line in a plot of the conductivity as a function of the logarithm of time. Study of the behavior of the films as a function of the annealing temperature allows also the detection of a reversible part in the variation of the resistivity. This variation is found nonlinear as a function of the inverse of the absolute temperature. A large increase in the conductivity is also found over a 100°C range of temperature starting at 490°C and has been interpreted as recrystallization of the amorphous film. Further study will involve measurements of the density of states and of the carrier mobility in the amorphous phase, optical absorption measurements, and electron microscopy examination.

3.2 Amorphous Silicon Thin Films (AEC)

Personnel: C. J. Mogab and R. G. Block

Amorphous silicon thin films were prepared by electron beam evaporation onto room temperature substrates. Density measurements of as-deposited films revealed that it is possible to obtain films in conditions ranging from five to twenty-five percent less dense than bulk crystalline silicon, depending upon residual gas atmosphere and deposition rate.

The electrical conductivity of amorphous silicon was studied between room temperature and 700°C. The as-deposited resistivity varied between 100 and 200 ohm-cm. In the temperature range from 100 to 450°C, the films exhibited a large irreversible decrease in conductivity similar to that observed for other amorphous semiconductors such as germanium, tellurium, and silicon carbide. The kinetics of this irreversible annealing phenomenon obeyed a logarithmic rate law as predicted by Primak's analysis of thermally activated processes distributed in activation energy. Analysis of the kinetic data yielded an activation energy range for annealing of about 0.5 to 2.0 eV. The fact that a distribution in activation energies is needed to describe the annealing kinetics is consistent with the assumption that the large irreversible changes in conductivity occur as a result of a variety of structural changes tending toward increasing internal order.

Crystallization of amorphous silicon occurred over a wide range of temperatures (500-700°C) and was accompanied by an irreversible increase in conductivity with time was found to follow the Johnson-Mahl-Avrami relations for nucleation and one-dimensional (rod-like) growth.

3.3 Relaxation Phenomena in Simple Glass-Forming Liquids (AEC)

Personnel: D. R. Uhlmann; W. T. Laughlin

Isothermal volume relaxation measurements in the vicinity of the glass transition have been made on three organic glass-forming liquids: α-phenyl, o-terphenyl and glycerin. The time dependence of volume relaxation in all three of these materials was found to be complex. For a given pair of temperatures, the form of the relaxation curves of samples quenched down in temperature was different than those quenched up in temperature. A form of Primak's distributed activation energy analysis has been applied to the volume relaxation data and the derived energy distributions were found to depend on temperature, shifting to higher energies with decreasing temperatures.

3.4 Phase Separation and Density of Glasses (AEC)

Personnel: D. R. Uhlmann

The variation of bulk density with composition across a miscibility gap has been described by a simple model in which volume additivity of the two phases was assumed. The density-weight percent composition function was found to have positive (concave-upward) curvature across a two-phase region. The density-mole percent composition function could have either positive or negative curvature, depending upon the location of the miscibility gap in the binary diagram and upon the molecular weights of the end-member oxides.

The model has been used to predict possible immiscible regions in the systems: K_2O-SiO_2, PbO-SiO_2, B_2O_3-GeO_2, SiO_2-GeO_2, PbO-GeO_2, and PbO-P_2O_5. Immiscibility is probably not present on the GeO_2-rich side of the alkali germanate series of glasses, while the LiF-rich limit of the miscibility gap in the LiF-BeF_2 system has been estimated.

4.0 Materials Synthesis and Preparation

4.1 Growth of Zinc Sulfide Crystals by Iodine Transport (AEC)

Personnel: B. J. Wuensch; P. N. Dangel

Transport of zinc sulfide by iodine in a closed system was studied to determine the kinetics of chemical transport processes. Crystals of ZnS of millimeter dimensions were successfully synthesized. The amount of mass transported was found to vary linearly with time, temperature gradient, and transport chamber diameter, in accord with the predictions of a simple diffusion-controlled model. The dependence of transport rate on transport agent concentration followed the kinetics of the diffusion model only at high I_2 concentrations. At lower concentrations the kinetics appeared to be limited by a finite surface reaction rate, and at still lower concentrations asymptotically approached the rate of sublimation-condensation. Although the sphalerite form of ZnS was the stable phase at all temperatures investigated, material transported at lower I_2 concentrations consisted of mixtures of wurtzite and sphalerite. Diffraction study of the crystals produced demonstrated randomness in the stacking sequence of the tetrahedral layers.

4.2 Freeze-Dry Preparation of Mixed Oxides (AEC)

Personnel: B. J. Wuensch; H. T. Anderson

The freeze-dry procedure consists of the spraying of an aqueous solution of salts of the desired cations into a bath of a cooled organic liquid, such as hexane, with which water is immiscible. The frozen droplets are removed, dried in vacuum, and subsequently calcined. Since the initial salts have had no opportunity to segregate, the resultant oxide is extremely homogeneous. An apparatus for the preparation of oxides by this technique has been successfully used in the preparation of magnesium gallate spinels of controlled stoichiometry. The procedure will shortly be used to synthesize nonstoichiometric oxides of the anti-fluorite structure type.

4.3 Development of A Transparent Furnace for Use in Crystal Growth (AEC)

Personnel: W. D. Kingery; C. Goodwin

Research has mainly been oriented toward building a small transparent furnace for use in growing crystals using the vapor flow, chemical deposition method. The motives for such a furnace are that growth conditions can be studied visually, thus achieving an understanding of the specific problems involved so that improvements may be made in a particular growth mechanism.

This furnace is constructed using an 80 mm Pyrex tube, the inside surface of which is coated with a gold film that acts as a specular mirror to a majority of the heat radiating from the source inside the tube. Such a gold layer reflects most of the infrared wavelengths, but is thin enough to allow a considerable portion of the visible to be transmitted, thus allowing visual monitoring.

To date, the gold layer has been applied by coating the glass surface with a metallo-organic solution of gold and heating the tube in an oxidizing atmosphere to about 500°C in order to burn off the volatile consitutents. However, this method has the disadvantage that layer uniformity is very difficult to obtain. Hence, the evaporation of the gold from a wire hung along the axis of the tube, using a vacuum system, is now being investigated.

Since temperatures of around 950°C will be needed for the crystal growth, methods of obtaining this without excessively heating the outer surface of the Pyrex tube are being studied. Also, different arrangements of the heating elements are under investigation, in order to obtain a step-function type temperature profile within the furnace.

4.4 Flow Apparatus for Growth of Single Crystals (AEC)

Personnel: W. D. Kingery; C. Seaton

Work has been initiated on a dynamic flow apparatus for growing single crystals. When completed, this equipment will enhance the crystal growth capabilities of the Ceramics Division. Initial emphasis will be placed on growth of single crystals of ZrO_2 and this program may be expanded into growth of ZrO_2-MgO solid solutions.

4.5 Solid Solution Single Crystals of Magnesia (AEC)

Personnel: W. D. Kingery; J. R. Booth

Single crystal MgO has been grown epitaxially on an MgO single crystal substrate. This growth was achieved by a static growth method which involves encapsulation of the reactants within a two-zone temperature gradient. The preliminary runs have been conducted at temperatures below the solubility limit of Al_2O_3 in MgO. To achieve the desired temperatures, encapsulation materials and procedures must be modified, or growth must be accomplished in a dynamic system. Future work will be done at temperatures where solid-solubility of Al_2O_3 in MgO is appreciable.

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R. G. Block, "Amorphous Silicon Thin Films," S.M. Thesis, Department of Metallurgy and Materials Science, September 1969.

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P. N. Dangel, "Growth of Zinc Sulfide by Iodine Transport," Ph.D. Thesis, Department of Metallurgy and Materials Science, September 1969.

R. N. Katz, "Dislocations Behavior in Alkaline Earth Fluorides," Sc.D. Thesis, Department of Metallurgy and Materials Science, September 1969.

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XIII. POLYMERS AND GLASSES

Faculty:

D. R. Uhlmann, Associate Professor, Metallurgy and Materials Science

Graduate Students:

P. D. Calvert, Research Assistant

M. Cukierman, Fairchild Camera and Instrument Corp. Fellow

R. W. Hopper, American Optical Co. Fellow

J. B. Park, Research Assistant

M. Tsai, Owens-Illinois Fellow

Personnel who have left:

J. B. Park (now at University of Utah)

Degrees Granted:

J. B. Park, S.M., Metallurgy and Materials Science, June 1969

Sponsorship:

Advanced Research Projects Agency, SD-90 DSR 75127

Research Report

1.0 Time-Dependent Properties of Glass-Forming Systems

Personnel: Professor D. R. Uhlmann; R. M. Kimmel

The description of kinetic processes distributed in activation energy has been applied to a variety of relaxation phenomena in amorphous materials. The relaxation phenomena include annealing of densified glasses (SiO_2 and polymethyl methacrylate); volume relaxation (polystyrene, polyvinyl acetate and glucose); time-dependent mechanical properties (polymethyl methacrylate); and recovery of deformed polymers (polystyrene). The results of these analyses have reflected the complexity of the relaxation kinetics. The corresponding distributions of activation energies have been derived and compared with energetic characteristics of other kinetic phenomena in the materials.

The first approximation analysis for deriving activation energy spectra from relaxation data, derived originally for linear distribution relaxation processes, has been shown to be valid as well for non-linear distributed processes. The analysis has also been applied to non-linear undistributed processes and found to indicate a spectrum of activation energies

with a maximum at the characteristic energy of the single process. The characteristics of spectra resulting from non-linearities have been considered, and procedures for evaluating the possible physical significance of derived activation energy spectra have been developed.

2.0 Deformation of Amorphous and Semi-Crystalline Polymers

Personnel: Professor D. R. Uhlmann; J. B. Park

The deformation of amorphous and semicrystalline polymers is being investigated. Emphasis is being placed on the relation between the mechanical properties and various structural and microstructural characteristics of the materials. Particular concern is being directed to various crystallization and orientation parameters, and their relation to the deformation process. The polymers presently being investigated include polyethylene, polypropylene, nylon, polycarbonate, and polystyrene.

3.0 Recovery of Deformed Polymers

Personnel: Professor D. R. Uhlmann; J. B. Park

The recovery of deformed polymers, both amorphous and semi-crystalline, is being investigated. The materials investigated to date include amorphous polycarbonate and semi-crystalline polythylene and polypropylene. Samples of polycarbonate were observed to recover completely at temperatures in the vicinity of the glass transition and above, while samples of polyethylene and polypropylene recovered only 90-95% of the initial strain even at temperatures within a few degrees of their respective melting points.

From the kinetics of recovery for each of these materials, activation energy spectra have been derived. The location in energy of these spectra has been found independent of the extent of deformation, but varied somewhat with the recovery temperature. The energy ranges covered by the spectra were 22 to 26 kcal/mole for polycarbonate; 22 to 24 kcal/mole for polyethylene; and 14 to 17 kcal/mole for polypropylene.

On repeated cold-drawing and isothermal annealing, the yield stress of completely-recovered polycarbonate decreased, while the mean activation energies for recovery remained about the same as on the first drawing and recovery. Similar behavior was observed for incompletely recovered polyethylene and polypropylene.

Studies of entropy annealing on the deformed polymers have also been carried out. The entropy changes on deformation were observed to anneal out in the same temperature range as the length changes. Activation energy

spectra were calculated from the kinetic data on entropy annealing; and the mean activation energies for entropy annealing were found to be about the same as those for strain recovery.

4.0 Crystallization of Polymers under Pressure

Personnel: Professor D. R. Uhlmann; P. D. Calvert

The crystallization of a number of polymers under high pre-sure has been shown to result in an extended-chain crystalline conformation, in contrast with the usual folded-chain conformation commonly observed in atmospheric pressure crystallization. The origin of this extended-chain morphology is presently being investigated, as is its effect on mechanical properties. Initial studies of the crystallization behavior have indicated that the growth of extended-chain crystals can take place quite rapidly at high pressure, and that the observed extended-chain crystals do not reflect merely a large-scale annealing of folded-chain crystals.

5.0 Crystallization of Polymers

Personnel: Professor D. R. Uhlmann; P. D. Calvert

The effect of crystallization conditions on the morphology of semi-crystalline polymers is being investigated, with initial attention being directed to polyethylene and polypropylene. Studies of crystallization in an imposed thermal gradient have shed light on the process in which radiating crystalline arrays are converted into highly oriented uniaxial arrays, and also indicated the importance of stray nucleation ahead of advancing crystal-liquid interfaces in affecting the final microstructure.

6.0 Theory of Diffuse Interfaces and Particle Coalescence

Personnel: Professor D. R. Uhlmann; R. W. Hopper

The theory of diffuse interfaces is being extended to treat finite systems containing more than a single interface. Preliminary results indicate that surface energy provides a driving force for particle coalescence, and that such coalescence can take place in reasonable times relative to experimental observations.

The work on particle coalescence is presently being continued in considering the effect of higher order terms in the free energy expansion employed. Also being considered is the effect of various higher order terms on the kinetics of spinodal decomposition.

7.0 Crystallization and Melting in Glass-Forming Systems

Personnel: Professor D. R. Uhlmann; M. Tsai

Studies of crystallization and melting in glass-forming systems can provide important information for elucidating the general nature of crystal growth from the melt. Studies carried out to date have indicated that for materials with large entropies of fusion ($\Delta S_f > 4R$), the crystal-liquid interface is faceted under all conditions of growth and non-faceted in melting; the interface site factor increases with increasing undercooling; and marked anisotropy is observed in the rates of crystallization and melting in the vicinity of the melting point. In contrast, for materials with small entropies of fusion, the interface morphologies are observed to be nonfaceted under all conditions of growth and melting, the interface site factor is independent of undercooling or superheat, and the curves of melting rate and crystallization rate are continuous with the same slope through the melting point.

Presently being investigated are the kinetics of crystallization and melting in both simple organic and inorganic oxide glass-forming materials. Emphasis is being directed to the effects of impurities on the kinetics of crystallization and melting and on the interface morphology.

8.0 Phase Separation in Glass-Forming Systems

Personnel: Professor D. R. Uhlmann

The phenomenon of liquid-liquid immiscibility is widespread in glass-forming systems. Previous studies in this laboratory and elsewhere have indicated phase separation in all the alkali and alkaline earth borates, in two alkali silicate systems, in all alkaline earth silicates, in the system SiO_2-B_2O_3, and in many of the commercially important ternary and more complex systems. In some cases, the morphology consists of isolated particles of one phase in a matrix of another phase, while in other cases two phases may be 3-dimensionally interconnected.

The origin of these interconnected submicrostructures is presently the subject of much discussion. In attempting to differentiate between spinodal decomposition on the one hand and nucleation, growth and coalescence on the other, studies are now being carried out in which electron microscopy is combined with small angle x-ray scattering and light scattering to elucidate the kinetics and the general chronology of submicrostructural development.

Also being considered are the effects of phase separation on the properties of glasses. Attention has thus far been directed to density and thermal expansion coefficient, while future work will be concerned with various conductive properties.

9.0 Flow and Relaxation in Simple Liquids

Personnel: Professor D. R. Uhlmann

Recent studies in this laboratory of viscous flow in simple organic liquids have indicated that the temperature dependence of the flow behavior is more complex than is envisaged by any of the standard theoretical models. At the same time, studies in inorganic oxide liquids have indicated a stress dependence at high stress levels which also is not in accord with theoretical expectations. Studies of volume relaxation in the vicinity of the glass transition have indicated a behavior which likewise is complex but from which activation energy spectra for the relaxation process could be derived. In the theoretical area, progress has been made in the initial formulation of a potential energy model flow.

The experimental results on flow and relaxation behavior are now being extended to even simpler liquids, while the theoretical development is directed toward treating in a more satisfactory fashion the cooperative nature of the flow process at relatively low temperatures.

10.0 Structure of Glasses

Personnel: Professor D. R. Uhlmann; M. Cukierman; Professor B. E. Warren, Department of Physics (ret.)

Recent advances in both experimental techniques and means of analysis have brightened the prospects for more definitive diffraction studies of glass structure. Previous studies utilizing the new techniques have been directed toward the elucidation of the structure of SiO_2 and B_2O_3.

These techniques are now being applied in diffraction studies of a number of simple glasses. The principal thrust of these studies is a determination of the structural state of the common modifying cations in glasses, the effect of cation additions on the framework structure, and the relation between the structural characteristics and various properties of the glasses.

11.0 A Study of Anomalous Water

Personnel: Professor D. R. Uhlmann; Professor D. Turnbull (Harvard)

A new form of water, variously called anomalous water or polywater, has recently been reported by investigators both here and abroad. This form of water, which is prepared by condensing at slight under-saturations in glass capillary tubes, is reported to have unusual properties, including a boiling point as high as 200°C, a density as high as about 1.3, and a glass transition temperature about -40°C.

This form of water is presently being investigated, with the object of establishing the role - if any - of impurities on the reported properties and improving our understanding of the structure - properties relation for this material.

Thesis

J. B. Park, "Deformation and Annealing of Amorphous and Semi-Crystalline Polymers", S.M. Thesis, Department of Metallurgy and Materials Science, June, 1969.

Publications:

R. M. Kimmel and D. R. Uhlmann: "On the Energy Spectrum of Densified Silica Glass", Phys. Chem. Glasses 10, 12 (1969).

R. M. Kimmel and D. R. Uhlmann: "Activation Energy Spectra for Relaxation in Amorphous Materials: I. Volume Relaxation in Polystyrene and Polyvinyl Acetate", accepted for publication, J. Appl. Phys.

P. D. Calvert and D. R. Uhlmann: "Thermal Effects of Shear in Opposed Anvil High Pressure Devices", accepted for publication, Am. Mineralogist.

XIV. X-RAY AND ELECTRON OPTICS LABORATORY

(Personnel from Department of Metallurgy and Materials Science except where indicated)

Faculty:

R. E. Ogilvie, Professor

Research Staff:

A. Saffir, DMD, Post Doctoral Fellow, Nutrition and Food Sci.
L. Sutfin, DDS, Post Doctoral Fellow, Nutrition and Food Sci.

Graduate Students:

J. S. Duerr, Research Assistant
W. K. Jones, Teaching Assistant
C. Lyman, Teaching Assistant

Support Staff:

J. A. Adario, Technician
J. I. Herman, Technician
Peggy Carney, Secretary

Sponsorship:

National Aeronautics and Space Administration, NsG-496 (part), DSR-70479
Office of Naval Research, NR-105-094, DSR-77590
National Institute of Dental Research, DE-105, DSR 71687
Smithsonian Astrophysical Observatory

Research Report:

1.0 Study of Metallic Meteorites

Personnel: J. S. Duerr
Sponsorship: Smithsonian Astrophysical Observatory

Research has continued in an effort to more fully define the thermal-mechanical history of metallic meteorites. The specific goal in the present work is to determine the role of

each of several possible phase transformations in the formation of plessite and the temperatures at which such transformations occur for the composition and cooling rates representative of metallic meteorites. A number of meteorites have been selected from the different classifications based on bulk nickel content, Ga-Ge content, and cooling rate. The plessite areas in each sample are being analyzed with the electron microanalyzer to determine nickel and carbon concentration profiles. For this study an automated stepping system was constructed for the electron microanalyzer to facilitate the carbon analysis. The sample is automatically traversed a set distance, a delay period is introduced to allow removal of surface carbon contamination, and the nickel and carbon X-ray intensities are recorded by typewriter.

2.0 Non-Dispersive X-ray Analysis With the Scanning Electron Microscope

Personnal: L. Sutfin
Sponsorship: National Institute of Dental Research; Office of Naval Research

The aim of this work is to improve on the spatial resolutions that are obtainable with the conventional electron microanalyzer.

Techniques for improving the efficiency of X-ray detection are being developed for use in analyses in which volumes with submicron dimensions are of interest. This is necessary if elemental distributions within cells and the nature of intracellular organelles are to be studied. The scanning electron microscope will be utilized for visualization and excitation of the sample. Non-dispersive analysis of X-ray spectra is being employed. Emphasis is being placed on light element detection.

Both a lithium drifted silicon detector and a gas flow proportional counter are being used to detect X-ray signals generated. The detection covers Be Kα through the maxium energy excited by the 20 KV beam. Energy resolution ranges from 180 ev for Be Kα to 620 ev for photons with energies near 20 KeV. The output is displayed on a 1024 channel analyzer with spectrum stripping and intergration capabilities. Plotted, printed and

punched paper tape outputs are available.

The system is applicable to any material and analyses of As_2Se_3 - Sb_2Se_3 systems, failure analyses, and identification of phases in dental amalgam have been performed.

It should be possible to analyze microtome sections of biological material with a resolution of 1000Å. This would be one order of magnitude better than that done in conventional probe analysis.

3.0 Electron Energy Analysis in Electron Microscopy

Personnel: C. Lyman
Sponsorship: Metallurgy Department

An electron energy analyzer is being built for installation in a commercial 100 KV electron microscope. This analyzer can image electrons which have lost various amounts of energy upon passing through a thin specimen. To disperse the electron beam a triangular magnetic prism is incorporated between the objective and intermediate lenses of the microscope.

In the conventional microscope both elastically scattered and inelastically scattered electrons go through the objective aperature and contribute to the image. If the inelastically scattered electrons are removed, chromatic aberration is minimized and the contrast is improved. This decrease in chromatic aberration would be helpful in the analysis of biological specimens and would also aid in the imaging of lattice planes.

An image may also be formed solely by electrons with the plasma energy loss characteristic of a certain element of compound; the brightness of the image being dependent upon the concentration of the element or compound. High resolution microanalysis on the order of 100 Å can be performed with this technique.

4.0 Dynamic Studies at Temperature on the Scanning Electron Microscope

Personnel: W. K. Jones
Sponsorship: Metallurgy Department

Because of the large depth of field and high resolution the S.E.M. is being utilized to study dynamic kinetic reactions. A hot stage, capable of 1000°C, has been constructed and coupled with a visual recording system, allows kinetic reactions to be studied as they occur.

Sintering of metallic microspheres, as an example, can occur by four possible mechanisms: evaporation-condensation, surface diffusion, viscous flow, and bulk diffusion. Research in the field has primarily been concerned with determining the primary mechanism for the material studied. Using the dynamic approach and the high magnification which can be obtained with the scanning electron microscope, we hope to obtain a better understanding of the rate controlling mechanism during the various stages of sintering.

Besides sintering, other topics of interest include phase transformations and high diffusivity mechanisms. Pearlite transformation, in both hypo and hypereutectic steels, is currently being investigated.

5.0 Biological Applications of the Electron Microprobe

Personnel: A. Saffir
Sponsorship: National Institute of Dental Research; Office of Naval Research

By developing methods to overcome multiple order spectral interference we have improved the capability of the electron beam microanalyzer to permit the analysis of fluorine in the presence of phosphorus and to accurately measure the Ca/P ratio in biological specimens. Our technique consists of measuring several independent signals from the several elements in spectral interference by employing pulse height analysis.

The unique capabilities of the instrument were utilized to study the relationship between dental caries susceptability, tooth chemistry and diet. Within a few days after eruption as much as 1,000 ppm of fluorine is to be found within 2μ of the surface of the tooth and this concentration decreases more than five fold at a depth of 10μ.

We have also observed that TMP (trimetaphosphate), a dietary cariostatic agent, enhances the maturation of young post-

eruptive surface enamel by increasing the Ca/P ratio.

Publications:

L. V. Sutfin, R. E. Ogilvie, R. S. Harris, "Selections of Optimum Pulse Height Analysis Window", 4th Nat'l. Conf. on Electron Microprobe Analysis, 1969.

R. E. Ogilvie, "Quantitative X-Ray Analysis With the Scanning Electron Microscope", Proceedings of the 2nd Annual Scanning Electron Microscope Symposium, 1969.

J. S. Duerr, J. Adario, R. E. Ogilvie, "Automated Stepping System for Carbon Analysis", Proceedings of the 4th Nat'l. Conf. on Electron Microprobe Analysis, July, 1969.

A. J. Saffir, R. E. Ogilvie, R. S. Harris, "Electron Microanalysis of Fluorine in Teeth", Programs and Abstracts of the Int'l. Assoc. of Dental Research, March, 1969 (47th Gen. Meeting)

S. N. Kreitzman, A. J. Saffir, R. S. Harris, R. E. Ogilvie, "Scanning Electron Microscopy of 'Dental Caries' Produced Enzymatically in-vitro", Proceedings of the 4th Nat'l. Conf. on Electron Microanalysis, July, 1969.

A. J. Saffir, R. E. Ogilvie, R. S. Harris, "Simultaneous Multi-Element Analysis with a Single X-ray Spectrometer", Proceedings of 4th Nat'l. Conf. on Electron Microanalysis

XV. NUCLEAR MATERIALS LABORATORY

Faculty:

T. O. Ziebold, Associate Professor of Nuclear Materials, Nuclear Engineering

Graduate Students:

F. Berte, Graduate Student
J. N. Lamb, Research Assistant and Graduate Student
G. R. Odette, Research Assistant and Graduate Student
K. Ohmae, Research Assistant and Graduate Student
G. B. Olson, Graduate Student

Support Staff:

J. Adario, Technician, Metallurgy
J. Herman, Technician, Metallurgy
Peggy Carney, Secretary, Metallurgy

Degrees Granted:

T. P. Hulick, S. M., Nuclear Engineering, & Naval Engineering June 1969

Sponsorship:

Office of Naval Research, N00014-67-A-0204-0013, DSR 70591
Office of Naval Research, PO 628-79-128/69, DSR 71638
National Science Foundation, GK-1768, DSR 70588
Atomic Energy Commission, AT(30-1)-4050, DSR 71517
Sloan Basic Research Fund, DSR 27690

Research Report

1.0 Influence of Impurities on the Radiation Embrittlement of Steels

Personnel: K. Ohmae
Sponsorship: Office of Naval Research

After a series of experiments at NRL on the study of radiation embrittlement in structural steels, particularly of the influence of individual and combined impurities, it was discovered that laboratory pure A302-B steel shows no transition temperature shift after an exposure of $\sim 10^{19}$ not (>1MeV). Addition of 200 ppm sulfur, however, caused the upper-shelf energy to drop down to one half of that of free heat, although the transition temperature after irradiation did not change at all. Phosphorus on the other hand exhibited a remarkable transition temperature shift (~80°C) after an exposure of 10^{19} not.

Fracture surfaces of these Charpy-V impact test specimens were carefully observed by the scanning electron microscope (SEM) and by the electron probe X-ray microanalyzer. Although the SEM gave us some indication of the change in fracture mode by irradiation, it was found to be difficult to characterize such a change in terms of fractography by the ratio of trans-intergranular fracture at lower temperatures or by the size and depth variation of the dimples of tear fracture at higher temperatures.

The electron probe, in turn, has provided useful information as to how the impurities are distributed in the matrix of A302-B steel in question. Essentially all sulfur added to this steel, which contains about 1.4% manganese, was found to form manganese sulfide stringers, and no sulfur was detected in the general matrix. The 300 ppm (by wet chemical analysis) was found to be distributed homogeneously in the steel; that is, no appreciable phosphorus segregation was detected by the probe (X-ray resolution on the order of a few microns). The mechanism of radiation embrittlement due to impurities was sought in this very difference of impurity distributions; i.e., either segregated or homogeneously distributed. The former probably has little effect on the embrittlement, because the impurity atoms (sulfur) are tied up within and the chance interaction between the

radiation induced defects and the impurity atoms is limited. The latter (phosphorus type), being uniformly distributed would inter act with the neutron-induced defects and form rather small defect clusters, which would cause the dislocation movement or the increase in the lattice friction term, σi, in the Petch equation. Efforts are being made to classify various impurities into two catagories described above and experimentally verify the interaction of uniformly distributed impurities with the radiation induced defects.

2.0 Spectral Analysis as a Means of Investigating Neutron Induced Hardening Detects

Personnel: G. R. Odette
Sponsorship: Office of Naval Research

Considerable progress has been made in the last year at MIT in an effort to relate basic radiation damage mechanisms to the experimentally observed damage energy dependence.

The experimental portion of the work consists of the irradiation of tensile test specimens in various reactor spectra while keeping other experimental variables constant. Suitable manufacturing and testing techniques for small pure iron and pure nickel tensile wires have been developed. A fast flux survey of the MITR vertical irradiation facilities and a preliminary irradiation of test samples to establish necessary exposure levels and handling and testing techniques were made.

Irradiation packages to keep the specimens cool (<100°C) and dry have been designed and constructed for seven irradiation locations - three at IRL, three at the MITR, and one at the NCR. All the longterm irradiations (5) have been completed and unpacking of the cans will begin at NRL soon.

Techniques for the measurement at the neutron flux and spectra in the various irradiation facilities are being developed. This will be done using a set of ten to fourteen threshold and resonance activation foil materials. Procedures for counting the foils have been established. Preliminary measurements using five foils showed results close to those expected at energies above 1 meV, and more extensive runs are being made currently. Short term tensile irradiations (< 1 week) will be run as soon as

fully tested foil packets are available.

Much effort has gone into methods to reduce and analyze the data generated in the experiment. The GAML computer code is being used to reduce the activation data to a suitable form. This data is then fed into SAND II, which was obtained from ORNL and is now running on the MIT 360-65. SAND II is used to unravel the neutron spectra from the saturation activities foil cross sections and an initial guess. The input guess is generated by the reactor physics transport code ANSIN. Other approaches to unfolding neutron spectra from foil measurements are being pursued at MIT and it is hoped that these will be used in this work.

SAND II is being modified to attempt to unfold an experimental damage response function from the measured spectra and changes in tensile properties. These damage functions will be compared to analytical functions.

Work has continued on the generation of analytical damage response functions for various defect models which hopefully span the range of probabilities. Programs for these calculations have been developed to a higher degree of sophistication, reflecting such influences as inelastic and nonistropic elastic scattering. Possible detailed knockon energy loss behavior and possible damage zone configurations predicted by computer simulations, both before and after thermal and mechanical rearrangements. Curves for a whole range of possible situations will be constructed.

The next few months will see the mechanical testing of the irradiated wires, irradiation and counting of foil packets in all the experimental locations, and the use of SAND II to unravel the neutron sprctra. An exhaustive series of runs using the modified SAND II will be made to compare the analytical models with the experimental data will be undertaken. The results of these tests will be studied in terms of the damage defect, including its generation, rearrangement and interaction with dislocations to produce mechanical property changes. Hopefully this will help clarify the basic nature of fast neutron radiation damage.

3.0 MIT Reactor Cryostat Design

Personnel: F. J. Berte
Sponsorship: National Science Foundation

An in-pile cryogenic irradiation facility is being constructed for the MIT Reactor. The cryostat will be located in the central fuel element of the reactor, where the neutron flux is approximately 17×10^{13} (neutrons/cm^2 sec.). Sample temperatures in the cryostat as low as 5°K will be maintained by use of a liquid helium refrigerant. An out-of-pile test cryostat has been constructed and is now being used to evaluate heat transfer performance and various safety parameters prior to the final fabrication and installation of the in-core cryostat.

It is intended that this in-reactor cryostat will be a central facility available to all MIT faculty and students interested in low temperature radiation damage studies.

4.0 Microcracking in Welds of Nickel Base Alloys

Personnel: J. N. Lamb
Sponsorship: Atomic Energy Commission

The electron microprobe has been used to study the redistribution of alloy elements near fusion welds of nickel base alloys. Microckacking during welding has been previously shown to be caused by grain boundary liquid film of unknown origin. Microprobe data permits quantitative measurement of alloy segregation in grain boundaries. Recent work has shown that grain boundary segregation is caused by solidification of a two-phase structure near the weld molten zone.

5.0 Simulation of High Neutron Flux

Personnel: T. P. Hulick
Sponsorship: Office of Naval Research

It is known that defects are produced in a crystalline solid when the crystal is exposed to bombardment by energetic neutrons. Semiconductor material is especially sensitive to

irradiation when used as a semi-conductor device since minute physical changes in a semi-conductor can cause large electrical changes. As nuclear reactors of higher fast neutron fluxes are developed (10^{16}n/cm^2/sec and above), first hand experiments in these flux ranges on irradiational behavior of semi-conductor material will be possible. The effects of very high neutron flux bombardment on semi-conductor material at room temperature can be simulated by irradiation at the liquid helium temperature and annealing at room temperature.

The time of irradiation at 4.2°K, the transit time in heating the semi-conductor material to room temperature or some other desired elevated temperature, the length of time that the specimen is held at the annealing temperature and the length of time involved in cooling the sample back down to 4.2°K must all be controlled according to the experimenter's specifications. Also, some property of the sample must be constantly monitored so that the appropriate changes in the chosen property can be observed. The physical property most easily measured remotely is electrical resistance or resistivity.

The design of a satisfactory semi-conductor holder, a sample heater, and ohmic contact for continued in-pile usage that can withstand hundreds of repeated heating-cooling cycles from 4.2°K to 270°K and the associated instrumentation necessary to provide controlled heating and cooling of the sample and continuous monitoring of resistance of the semi-conductor sample are the accomplishments of this thesis.

Publications:

H. F. Bowman, J. L. Smith, Jr., and T. O. Ziebold, "The Influence of Nuclear Radiation of Pool-Boiling Heat Transfer to Liquid Helium", Trans. ASME, (preprint 68-WA/PID 3).

H. F. Bowman, T. O. Ziebold and J. L. Smith, Jr., "Low Temperature Thermal Conductivity of Copper Irradiated with Reactor Neutrons," Proc. Eighth Conf. on Thermal Cond., 1969.

MATERIALS ENGINEERING

I. MECHANICS OF DUCTILE FRACTURE

Faculty:

F. A. McClintock, Professor, Mechanical Engineering
A. S. Argon, Professor, Mechanical Engineering
C. A. Berg, Associate Professor, Mechanical Engineering

Graduate Students:

J. W. Carson, Research Assistant, Mechanical Engineering
J. Joyce, Research Assistant, Mechanical Engineering
D. M. Tracey, Research Assistant, Mechanical Engineering
I. F. Stowers, Research Assistant, Mechanical Engineering
J. Delahanty, Undergraduate Assistant, Mechanical Engineering
J. Eckerle, Undergraduate Assistant, Mechanical Engineering
L. Miller, Undergraduate Assistant, Physics
R. Harrington, Undergraduate Assistant, Mechanical Engineering
C. Weissgerber, Undergraduate Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering (part time)
R. Leonard, Instrument Maker, Mechanical Engineering (part time)
R. M. Graudins, Secretary, Mechanical Engineering (part time)

Personnel who have left:

J. A. Joyce (Now at the Draper Laboratory, M.I.T.)
D. M. Tracey (Now at Brown University, Providence, R. I.)

Degrees Granted:

J. Tirosh, Sc.D., Mechanical Engineering, June 1969
I. F. Stowers, M.S., Mechanical Engineering, September 1969
R. Harrington, B.Sc., Mechanical Engineering, May 1969

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

Experiments on crack propagation from grooves under combined shear and tension show that although the fracture surface is formed by hole growth and coalescence, the material just beneath the surface is almost entirely intact. This indicates that as the crack grows, only the interaction with the next hole or two is important. Analysis and experiment both show that the holes at $\pm$ 45° rather than directly ahead of the crack are likely to be the important ones.

Experiments are being run on asymmetric, fully plastic specimens to determine the effect of kind of flow field at a given triaxiality.

2.0 Analytical Results

An anisotropic analysis has been developed for the plastic stress, strain, and displacement around cracks in highly anisotropic, uniaxially reinforced composites. For growing cracks in isotropic materials, the plastic zone has been modeled by two rows of edge dislocations, the rows parallel to the crack with Burgers vectors normal to the crack. The dislocations are added to these rows and are then left behind by the growing crack. The resulting residual stress seems to have small effect on the plastic zone, compared to that found by Chitaley for longitudinal shear parallel to the leading edge of the crack.

3.0 Numerical Results

The numerical solution of elastic-plastic and rigid-plastic problems by the superposition of stress fields of screw dislocations has to be completed for longitudinal shear with traction boundary conditions, and a user's manual is in preparation. A method has been formulated for treating general plane strain boundary conditions that are specified by a traction-displacement relation. Graphical techniques have been developed for computer plotting of

all components of plane strain fields, for easier comprehension of the results. This is particularly valuable in determining the rigid-plastic slip line fields from computer results, so that further development can be done analytically.

Theses:

J. Tirosh, "Stress and Strain in Elasto-Plastic Cracked Bar under Torsion and Longitudinal Shear," Ph.D., Department of Mechanical Engineering, June 1969.

I. F. Stowers, "Numerical Procedure for Tension Mode Elasto-Plastic Solution by Assembling Dislocations," S.M., Department of Mechanical Engineering, August 1969.

R. J. Harrington, "Fracture Toughness as Determined by Metallurgical Properties," B. Sc., Department of Mechanical Engineering, May 1969.

Publications:

H. W. Huff, J. A. Joyce, and F. A. McClintock, "Fully Plastic Crack Growth under Monotonic and Repeated Bending," Proc. 2nd Int. Conf. Frac., Fracture 1969, Brighton, England, 83-93, 1969, Chapman and Hall, Ltd.

F. A. McClintock, "Challenges in Fracture Mechanics," Proc. 11th Midwestern Mech. Conf., Developments in Mechanics, 5, 905-919, Iowa State Univ. Press, Ames, 1969.

F. A. McClintock, "Crack Growth in Fully Plastic Grooved Tensile Specimens," Phys. of Strength and Plasticity, Orowan Anniversary Volume, ed. by. A. S. Argon, 307-326, 1969, M.I.T. Press.

C. A. Berg, "Plastic Dilatation and Void Interaction," Inelastic Behavior of Solids, McGraw-Hill, (Colloquium of Battelle Memorial Institute, Columbus, Ohio, Sept. 15-19, 1969), (in press).

F. A. McClintock, "Plasticity Aspects of Fracture," Chapter in Fracture, by H. Liebowitz, Academic Press, (in press), 1969.

J. Tirosh, "A Direct Numerical Method for Stress and Stress Intensity Factor in Arbitrary, Cracked, Elastic Bars under Torsion and Longitudinal Shear," (submitted), 1969.

J. Tirosh, and F. A. McClintock, "Finding Elasto-Plastic Stress and Strain in Cracked Bars under Torsion and Shear by Assembling Screw Dislocations," (submitted), 1969.

C. A. Berg, "Principles of Virtual Work and Complementary Virtual Work for Cosserat Media," (submitted), 1969.

A. D. Chitaley, and F. A. McClintock, "Elastic-Plastic Mechanics of Steady Crack Growth under Anti-Plane Shear," (submitted), 1970.

II. PLASTIC DEFORMATION AND STRAIN HARDENING

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Research Staff:

A. P. Tanon, Visiting Engineer, Mechanical Engineering

Graduate Students:

G. H. East, Research Assistant, Mechanical Engineering
W. Wu, Research Assistant, Mechanical Engineering
T. Lundeen, Undergraduate Assistant, Mathematics

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering
R. Graudins, Secretary, Mechanical Enginering

Degrees Granted:

W. Wu, SM, Mechanical Engineering, September 1969

Sponsorship:

National Science Foundation Grant GK-3700, DSR 71350

Research Report

1.0 Easy Glide in Copper

A process for reducing dislocation densities to 10^3 per square cm. in copper single crystals having the easy glide orientation used in previous experiments has been perfected. In addition a precission constant stress creep machine has been developed with which thermal analysis of the rate mechanism in easy glide will be made. Sectioning and etching experiments for studying the mechanism of multiplication of secondary dislocations have also been started.

2.0 Strain Hardening in Tungsten

A high temperature-vacuum tensile frame has been developed for the

Instron machine and used in preliminary experiments on tungsten single crystals with a single slip orientation at 550°K and 850°K. The experiments showed that at 550°K the stress-strain curves are parabolic, and have the same general shape as at low temperatures. At 850°K the stress-strain curves exhibit three stages of deformation characteristic of f-c-c crystals and some b-c-c crystals. The results of a thermal analysis have shown that the rate mechanism is consistent with intersection of forest dislocations. Little evidence for the development of appreciable internal stresses was found. The wavy slip bands which are observed at 850°K correlate directly with a cellular dislocation structure inside the crystals which can be revealed by etch pits. Preliminary experiments of thin film transmission electron microscopy have been performed and will be expanded.

3.0 Thermally Activated Motion of Dislocations Through Random Obstacles

A statistical theory for the thermally activated motion of dislocations through random obstacles has been developed to explain previously obtained distribution functions of displacements of dislocations under stress pulses in NaCl. The theory is capable of successfully connecting externally observed distributions with internal details and is consistent with the model of overcoming some statistically overstressed obstacles followed by sideways unzipping of the average obstacles in between.

4.0 Plasticity in Glassy Materials

The possibility of dislocation motion in glassy materials was explored theoretically. Considering a glass as a concentrated solid solution of tetragonally misfitting particles makes it possible to calculate by means of the Ridhagni-Asimow Theory the stress necessary to displace a dislocation in a glass provided the width of the principal peak of X-ray radial distribution functions can be taken as a measure of the tetragonality strain. The calculated elastic shear strains at yield are 0.01 which falls considerably short of the measured yield strains of 0.1 - 0.15 in inorganic and polymeric glasses indicating that the yield strains of these materials are high because of an inherent lattice resistance to dislocation motion resulting from strong covalent bonding or configurational locking.

Theses:

W. Wu, "Plastic Deformation of Tungsten Single Crystals Between Room Temperature and 600°C", SM Thesis, Department of Mechanical Engineering, October 1969.

Publications:

A. S. Argon, "The Yield Strength of Glasses" Presented at the 4th Microsymposium on Macromolecules of the IUPAC in Prague, Czechoslovakia, September 1969, to be submitted to Materials Science and Engineering.

A. S. Argon, "Motion of Dislocations through Thermally Penetrable Random Obstacles", to be submitted to Phil. Mag.

A. S. Argon, and G. E. Padawer, "Plastic Deformation in NaCl Single Crystals", to be submitted to Phil. Mag.

III. PHYSICS OF STRENGTH AND PLASTICITY

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Sponsorship:

Grants from a) Air Force Office of Scientific Research, b) Army Materials and Mechanics Research Agency, c) General Electric Research Laboratory, d) Boeing Scientific Research Laboratory, e) Monsanto Research Laboratory, DSR 70936.

Research Report

Thirty seven of the world's leading authorities on mechanical behavior of materials were invited to provide theoretical contributions in the fields of fracture, dislocations, deformation and hardening mechanisms, in engineering and geological applications in honor of the retirement of E. Orowan.

Publications:

A. S. Argon, (Editor) "Physics of Strength and Plasticity", M.I.T. Press, in the press.

IV. MECHANISMS OF FATIGUE DAMAGE IN SEMI-BRITTLE MATERIALS AT ELEVATED TEMPERATURES AND FATIGUE IN COMPOSITES

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Research Staff:

R. Safoglu, Visiting Engineer, Mechanical Engineering

Graduate Students:

I. Choi, Research Assistant, Mechanical Engineering
D. H. Hunt, Research Assistant, Mechanical Engineering
Y. A. Patel, Research Assistant, Mechanical Engineering
R. N. Wright, Research Assistant, Metallurgy and Materials Science
R. Scanlan, Undergraduate Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering
R. Graudins, Secretary, Mechanical Engineering

Personnel who have left:

Y. A. Patel (now Research Assistant, Mechanical Engineering with Professor N. Cook)
R. N. Wright (now Alleghany-Ludlum Research Laboratory, Pittsburgh, Pa.)

Degrees Granted:

R. N. Wright, Sc.D. Metallurgy, January 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75109

Research Report

1.0 Fatigue Mechanisms in Semi-Brittle Materials at High Temperatures

A tungsten wire wound zirconia tube high temperature furnace built in a vacuum system was designed and built to be used for the constant load amplitude SF-2 Fatigue machine. Initial tests demonstrated that the temperatures

of 1600°C are readily achievable in slender cantilever fatigue specimens. Experiments on high temperature fatigue damage in MgO have been started to study the type of pore damage observed earlier in LiF. Further experiments on Al_2O_3 are planned.

2.0 Fatigue Mechanisms in Semi-Brittle Materials at Intermediate Temperatures

The high temperature (1000°C) vacuum system developed for the earlier LiF experiments has been converted for use with the Automation Industries, controllable displacement fatigue machine for the study of fatigue damage in antimony at devated temperatures. Presently experiments are in progress to determine the temperature dependence of the yield stress in antimony.

3.0 Fatigue in Laminates

Transparent laminates of glass and silver chloride have been prepared by melting thin sheets of rolled silver-chloride between microscope slides. It has now been possible to make transparent bubble free laminates of these materials having deliberately introduced transverse cracks in the glass sheets. The process of delamination by crack growth in the silver chloride to bridge the transverse cracks in the glass sheets is now being studied as a possible mode of fatigue damage in laminates and fibrous composites.

Theses:

R. N. Wright, "Fatigue Crack Propagation in Iron Silicon", Sc. D. Thesis, Metallurgy and Materials Science, January 1969.

Publications:

A. S. Argon, and J. A. Godrick, "Fatigue in Lithium Fluoride Single Crystals at Elevated Temperatures", Czech. J. Phys. B19, 341, (1969).

A. S. Argon, and J. A. Godrick, "Fatigue in Lithium Fluoride Crystals at Elevated Temperatures", Fracture 1969, Chapman and Hall Ltd., 576, (1969).

A. S. Argon, and R. N. Wright, "Fatigue Crack Propagation in Silicon Iron" to be submitted to the ASM Transactions.

V. MECHANICS AND PHYSICS OF DAMAGE IN COMPOSITE MATERIALS

Faculty:

C. A. Berg, Associate Professor, Mechanical Engineering
W. J. Shack, Assistant Professor, Mechanical Engineering

Graduate Students:

R. B. Melton, Jr., Instructor, Mechanical Engineering
A. Lew, Research Assistant, Mechanical Engineering
R. G. Hamilton, NSF Fellow, Mechanical Engineering
D. Hiatt, Research Assistant, Mechanical Engineering
A. Rinsky, Research Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering
Pamela Beecher, Secretary, Mechanical Engineering

Personnel who have left:

R. B. Melton, Jr. now in Denton, Texas
R. G. Hamilton, now with General Electric Gas Turbine Division
A. Lew, now with Sandia Corp. Livermore, Calif.

Degrees Granted:

R. B. Melton, Jr., Sc.D., Mechanical Engineering, June 1969
R. G. Hamilton, SM, Mechanical Engineering, Feb. 1969
A. Lew, SM, Mechanical Engineering, Sept. 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75110

Research Report

1.0 Fracture of Composites

The analytical and experimental investigation of the possible presence of multi-polar stress effects in composites (induced by the microstructure), and the possible influence of these effects on fracture was began last year. A. Lew investigated the effect of couple stresses -- the simplest

form of polar stress -- on the structure of singular deformation fields about notch tips, and gave a generalization of Williams' now classical stress intensity factor to characterize such singularities. R. Hamilton devised a set of experiments in which the singularities of stress and couple stress at notch tips are markedly different. He then carried out these experiments, using quasi-isotropic fiber glass laminates, and demonstrated that in these materials couple stress effects do not appear; also, Hamilton's experiments indicate that Williams' classical stress intensity factor, calculated on the assumption that couple stresses are not present, provides a sufficient basis for representation of fracture data. The question of whether higher polar stresses may be present in the materials is still open.

R. Melton and C. Berg, working in colaboration with Celanese Research Company Laboratories, undertook an experimental study of fracture in the grip section of unidirectional fiber reinforced tensile specimens. One product of this effort was the design of a new system of gripping tensile specimens to prevent grip fracture; grips for this purpose were fabricated and tested both at M.I.T. and at Celanese Laboratories. Another product of this study was identification of some of the basic features of shear fracture in glass fiber reinforced material. By studying electron micrographs of the shear fracture surfaces it was determined that shear fracture which takes place while no compression acts transverse to the fiber direction, occurs by peeling at the interface between the resin and the silane coating on the glass. Shear fracture produced under compression, on the other hand, proceeds through the resin matrix itself. These studies are being pursued further. In addition, the process of notch extension in composites is being studied by direct experimental observation to determine how much of presently available analysis of fracture processes (e.g. "fracture mechanics") may be applicable to characterization of fracture in composites.

Publications, Theses and Reports:

C. A. Berg, "Kinematic Reversibility in Plane Deformation of Nonlinear Fluids," Proc. 5th Internat'l Congress on Rheology, Kyoto, 1968.

C. A. Berg, "Conservative Behavior of Nonlinear Fluids in Two Dimensional Flow," Proc. 5th Internat'l Congress on Rheology, Kyoto, 1968.

C. A. Berg, R. Melton, T. Dunn, and I. Kalmin, "An Experimental Study of Fracture in the Grip Section of a Tensile Specimen," Fourth Annual Symposium on High Performance Composites at Washington University, St. Louis, April, 1969.

C. A. Berg, "Physically Based Compatibility Relations for Multipolar Media," Fourth National British Coloquium on Theoretical and Applied Mechanics, Nothingham England, March 31-April 2, 1969.

R. G. Hamilton, "The Effect of Couple Stress on the Initiation of Fracture in Composite Materials," M.S. Thesis, Department of Mechanical Engineering M.I.T., January 20, 1969.

A. Lew, "The Effects of Couple-Stresses on the Stress Singularities near a Crack Tip," M.S. Thesis, Mechanical Engineering, M.I.T., August, 1969.

VI. PROPERTIES OF FIBER COMPOSITES

Faculty:

J. Wulff, Professor, Class of 1922 Emeritus, Metallurgy and Materials Science

J. W. Mar, Professor, Aeronautics and Astronautics

Graduate Students:

O. Orringer, Graduate Student, Aeronautics and Astronatuics

G. Sedor, Graduate, Naval Architecture

R. Watterson, Graduate Student, Naval Architecture

Undergraduate Students:

W. Scott, Undergraduate Student, Aeronautics and Astronautics

J. Woneis, Undergraduate Student, Aeronautics and Astronautics

M. Pustejovsky, Undergraduate Student, Aeronautics and Astronautics

Personnel Who Have Left:

T. Courtney, Research Associate, Metallurgy and Materials Science (Now at University of Texas)

P. Dickenson, Graduate Student, Naval Architecture (Now with United States Coast Guard)

G. Garmong, Graduate Student, Metallurgy and Materials Science (Now at North American Rockwell Corp)

L. Shepard, Research Associate, Metallurgy and Materials Science (Now at Army Materials and Mechanics Research Center)

S. Weidenschilling, Graduate Student Aeronautics and Astronautics, (Now on active duty in the United States Army)

D. White, Graduate Student, Naval Architecture (Now with United States Coast Guard)

Degrees Granted:

R. Dickenson, S.M., Naval Architecture, May 1969

G. Garmong, Ph. D., Metallurgy and Materials Science, May 1969

D. A. White, S. M., Naval Architecture, May 1969

Sponsorship

Air Force Office of Scientific Research (OAR), AF 49 (638) - 1463, DSR 72002

Research Report

1.0 Size Effects in Fiber Composite Deformation

The dependence of the mechanical properties on fiber size and spacing of composites of Ferrovac E iron fibers unidirectionally aligned in an OFHC copper matrix was studied. Recrystallized composites containing 0.033 to 0.968 volume fraction fiber with fiber diameters ranging from 10 to 5 x 10^{-3} mils were fabricated and tested in tension at temperatures from 77°K to 373°K. The composite elastic modulus followed the prediction of the rule of mixtures, independent of fiber size and spacing. For composites containing less than 0.3 volume fraction fiber, matrix yielding and flow at low strains was described by the Orowan and Petch formulations of dislocation - obstacle interactions and were consequently strongly dependent on fiber size and spacing. Matrix flow stresses at 0.001 plastic strain of over 40,000 pounds per square inch were observed in composites of 0.01 mil fiber spacing. For composites containing greater than 0.6 volume fraction fiber, geometrical constraints inhibited matrix flow to stresses as high as 75,000 pounds per square inch.

A range of yield stresses for the iron fibers from 40,000 pounds per square inch to 300,000 pounds per square inch was observed due to the ability of the matrix to arrest the longitudinal propagation of individual yielded regions. Composite yielding was by the accumulation of individual fiber yields when large amounts of matrix were present and by the catastrophic growth of yielded regions when the fibers were closely spaced.

Composites which did not fail during yielding elongated by Luders deformation and subsequent hardening at levels determined by the strengths developed early in the straining. Composites tested at temperatures at which iron is normally brittle deformed plastically due to inhibition of the twining failure

mechanism of iron.

2.0 Electron Microscopy of a Fiber Composite

Specimens of a composite consisting of continuous fibers of Ferrovac E iron in a matrix of OFHC copper were observed by transmission electron microscopy. Fiber sizes of .005 mil and .01 mil at volume fractions of .033 and .069, respectively, were studied in the annealed state and at strains of 1/2% and 1%. An electrolytic thinning technique for specimen preparation was developed.

The specimens were found to have a very small matrix grain size, about .01 to .02 mil. Grain size was limited by fiber spacing. Fibers were preferentially located at the intersection of several grains, precluding the operation of an Orowan-type strengthening of the matrix by the fibers. No precipitation due to interdiffusion from the fibers during fabrication was found in the matrix.

Dislocation densities in the annealed specimens were low. No evidence of thermal strain due to differential expansion of the matrix and fibers was found. In the strained material, dislocation densities were high. No interaction of dislocations in the matrix with the fibers was observed. No dislocation substructure was found. The matrix strengthening and rapid work-hardening were attributed to grain size effects.

3.0 Continuous Casting of Eutectic Fiber Composites Sheets

A study was made of the potential for rapid growth of eutectic fiber composite materials. The feasibility and conditions for the production of unidirectionally aligned fiber composites from the melt were established recently by Mollard and Flemings. Furthermore, it was demonstrated by Marsh in an earlier study of this project that it is possible to grow an $Al-Al_3Ni$ eutectic fiber composite in configurations appropriate to rapid growth conditions.

In order to maintain a fiber structure with increasing growth rates, the ratio of temperature gradient in the liquid to growth rate (G/R) must be maintained constant. A high rate of heat extraction is required at the growing solid interface.

In addition the heat must be extracted along the fiber direction.

Initial attempts to produce fiber composite strips at high growth rates proved unsuccessful, though sufficient evidence was obtained to demonstrate the feasibility of the project. A second effort to produce the fiber-reinforced material in rod form proved easier to control and quite successful. The fastest growth rate for the Al-Al_3Ni fiber composite previously reported in the literature was about 30 cm/hour. In this work, a fiber composite was grown at 95 cm/hr with a fiber spacing of 0.9 microns. Yet higher rates are probably possible.

Although further work is required to determine the useful range of application for rapid eutectic fiber growth in composite production, it seems that this or similar processing methods will prove important in future applications.

4.0 The Effect of the Interface Compound on the Tensile Strength of an Aluminum Matrix - Boron Fiber Composite

A study was made of the effect of intermetallic compound formation upon the strength of aluminum matrix - boron fiber composites. Composites containing a 6 volume % of 4 mil boron fibers were prepared by vacuum infiltration.

Specimens were prepared to exhibit varying amounts of growth of the compound AlB_2 at the fiber - matrix interface. Samples heat treated in the solid aluminum matrix region showed no visible compound formation, although the boron fibers exhibited some attack after prolonged heating (64 hours at 600°C or 24 hours at 650°C). Compound formation did occur in samples heat treated above the melting point of the aluminum matrix (720° to 800°C and times from 5 seconds to 6 minutes). These latter samples were simply allowed to remain under the hot liquid aluminum bath after infiltration. These results are in keeping with the previously reported work by Wolff and Hill.

Tensile specimens prepared from the reacted samples showed roughly six tenths of the strength expected for the mixture rule value, if the calculation suggested by Heitman were used. In this calculation, the reduced volume fraction, i.e., the fiber area excluding the brittle compound formed, is used as a measure of volume fraction. A number of possible reasons for

the low observed strength include matrix voids, nonuniform fiber spacing, fiber alignment (though in most cases the alignment proved quite good) and possible nonuniform fiber strength with unreacted material.

Multiple fractures were observed in each individual fiber before composite failure, as was reported earlier by Heitman.

Theses:

R. Dickenson, "Continuous Casting of Eutectic Fiber Composite Sheets", S. M. Thesis, Department of Naval Architecture, May 1969.

G. O. Garmong, "Size Effects in Fiber Composite Materials", Ph. D. Thesis, Department of Metallurgy and Materials Science, May 1969.

S. J. Weidenschilling, "Electron Microscopy of a Fiber Composite", S. M. Thesis, Department of Aeronautics and Astronautics, July 1969.

D. A. White, "The Effect of Interface Compound on the Tensile Strength of an Aluminum Matrix - Boron Fiber Composite", M. S. Thesis, Department of Naval Architecture, May 1969.

VII. PHYSICAL AND CHEMICAL PROPERTIES OF FIBERS AND POLYMERS

Faculty:

S. Backer, Professor, Mechanical Engineering
I. V. Yannas, Associate Professor, Mechanical Engineering

Research Staff:

E. I. Valko, Senior Research Associate, Mechanical Engineering
R. C. Sheldon, Instructor, Mechanical Engineering

Graduate Students:

E. C. Ibe, Graduate Student, Mechanical Engineering
A. Maranci, Graduate Student, Mechanical Engineering
N-H. Sung, Research Assistant, Mechanical Engineering
S. Arghyros, Research Assistant, Mechanical Engineering
H. Patel, Graduate Student, Mechanical Engineering
D. Rice, Graduate Student, Mechanical Engineering
A. Crugnola, Graduate Student, Mechanical Engineering
A. Lunn, Research Assistant, Mechanical Engineering
R. Naar, Graduate Student, Mechanical Engineering
A. Eltayebi, Research Assistant, Mechanical Engineering
A. Shiekh, Graduate Student, Chemical Engineering
J. Shah, Graduate Student, Mechanical Engineering
T. Suraiya, Graduate Student, Mechanical Engineering
C. Huang, Research Assistant, Mechanical Engineering
Y. Kadman, Research Assistant, Mechanical Engineering

Support Staff:

D. Eastman, Secretary, Mechanical Engineering

Degrees Granted:

S. Arghyros, S.M., February 1969
N. K. Jain, S.M., February 1969
A. Maranci, S.M., February 1969
J. N. Shah, S.M., June 1969
T. Suraiya, S.M., September 1969
H. C. Patel, S.M., June 1969

Sponsorship:
Allied Chemical Corporation
Beaunit Corporation
Burlington Industries, Inc.
Department of Commerce, NBS CST-164, DSR 76268
Derby Foundation
E. I. du Pont de Nemours & Co., Inc.
Camille and Henry Dreyfus Foundation
Instron Corporation
Charles T. Main Company
Monsanto Corporation
National Institutes of Health, 1-Rol-AM11919-01, DSR 71218
National Science Foundation, GK-2024, DSR 70976
Phillips Petroleum Company
J. P. Stevens Company
West Virginia Pulp and Paper Corporation
Lawson-Hemphill Company

Research Report:

1.0 Bending Mechanisms in Textile Structures

Personnel: S. Backer, B. Hindman

This study is directed towards clarifying the role of interfiber friction on bending rigidity, bending hysteresis, and flexural resilience of twisted and woven structures.

2.0 Storage and Retrieval of Textile Information

Personnel: S. Backer, E. I. Valko, R. A. Roach

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. An extensive industry-cooperative experiment has been conducted in 1969.

3.0 Nonlinear Viscoelastic Behavior of Polymers

Personnel: I. Yannas, A. Lunn, N. Sung, S. Kornfeld, J. Shah

Studies of the nonlinear viscoelastic behavior of polymers are conducted in creep, stress relaxation, and at constant rate of extension. Amorphous polycarbonate and amorphous polyethylene terephthalate are the principal subjects of their study.

4.0 Physicochemical and Engineering Study of Collagen

Personnel: I. Yannas, S. Arghyros, A. Sheikh

The determination of mechanical and spectroscopic properties of collagen in various states of aggregation is the goal of this study.

5.0 Thermal Relaxation Phenomena in Polymers

Personnel: I. Yannas, N. Jain, A. Eltayebi

The isothermal relaxation of birefringence in polycarbonate and other synthetic polymers is under investigation.

6.0 Heat Setting of Nylon 6.6

Personnel: I. Yannas, J. Shah

A fundamental study of the heat setting process for Nylon 6.6 is conducted in the temperature range 100°-200°C in an effort to establish a quantitative basis for this well-known industrial process.

7.0 Direct Conversion of Chemical to Mechanical Energy

Personnel: I. Yannas, M. Turai, D. Mark

A polymer engine, which operates isothermally between two levels of the chemical potential, has been built and is currently under study in an effort to develop criteria for improvement of the properties of the working substance.

8.0 Diffusion in Crosslinked Cellulose

Personnel: E. I. Valko, E. C. Ibe

The diffusion of dyes in crosslinked cellulosic materials such as cotton, rayon and cellophane is investigated as an example of the influence of crosslinks on the diffusion of polymers in general.

9.0 Theory of Dyeing Synthetic Polymers

Personnel: E. I. Valko, E. C. Ibe, D. Rice

The theory of dyeing synthetic fibers by disperse dyes is interpreted in terms of the solubility parameter theory. Experiments are carried out to prove this hypothesis.

Theses:

S. Arghyros, "Dehydration of Soluble Collagen", S.M.,

Department of Mechanical Engineering, January 1969.

J. Shah, "The Heat Setting of Nylon 6.6", S.M., Department of Mechanical Engineering, January 1969.

D. Mark, "Optimizing Collagen Fibers for Use in a Collagen Engine", S.M., Department of Mechanical Engineering, August 1969.

T. Suraiya, "Local Heat Transfer Around a Cylinder in Cross Flow to Dil-Polymer Solution", S.M., Department of Mechanical Engineering, September 1969.

H. C. Patel, "Drafting Mechanics of Non-Homogeneous Fiber Blends", S.M., Department of Mechanical Engineering, June 1969.

A. Maranci, "Initial Modulus of Monofilaments and Wires in Axial Compression", S.M., Department of Mechanical Engineering, February 1969.

Publications:

H. R. Plonsker and S. Backer, "Dynamics of Drafting, Part II. The Role of Fiber Crimp in Tensile Behavior of Slivers at Low Drafts or Strains", Textile Research Journal 39, 823-829 (1969).

S. Backer and E. I. Valko, Thesaurus of Textile Terms, 2nd Edition, The M.I.T. Press, Cambridge, Massachusetts, April 1969.

S. Backer, J. W. S. Hearle, and P. Grosberg, "Structural Mechanics of Fibrous Materials", Interscience Publishers, New York, New York, September 1969.

J. J. Willard, G. C. Tesoro, and E. I. Valko, "Effect of Radial Location of Crosslinks in Cellulose Fibers on Fabric Properties", Textile Research Journal (in press).

C. J. Gogek, W. F. Olds, E. I. Valko, and E. S. Shanley, "Preswelling of Durable Press Performance of Cotton", Textile Research Journal (in press).

E. I. Valko, "Fundamental and Applied Research in the Field of Dyeing Processes--Survey of Achievements and Needs in the Textile Industry", Textile Research Journal 39, No. 8, August 1969.

C. J. Gogek, W. F. Olds, E. I. Valko, and E. S. Shanley, "Effect of Preswelling on Durable-Press Performance of Cotton", Textile Research Journal 39, NO. 6, June 1969.

J. J. Willard, G. C. Tesoro, and E. I. Valko, "Effect of Radial Location of Crosslinks in Cellulose Fibers on Fabric Properties", Textile Research Journal 39, No. 5, May 1969.

E. I. Valko, B. Bitter, and L. Gagnon, "Observations on Bleaching Wool", American Dyestuff Reporter, January 27, 1969.

I. V. Yannas, "Massive Internal Fracture of an Amorphous Polyester", Science 166, 227 (1969).

VIII. STRUCTURAL MATERIALS

Faculty:

F. J. McGarry, Professor, Civil Engineering
R. C. Jones, Associate Professor, Civil Engineering
F. Moavenzadeh, Associate Professor, Civil Engineering
S. P. Shah, Visiting Associate Professor, Civil Engineering

Research Staff:

C. B. Arends, Visiting Scientist, Civil Engineering
O. E. Gjorv, Research Associate, Civil Engineering
M. H. Gradowczyk, Research Associate, Civil Engineering
J. F. Elliott, Part-time Instructor, Civil Engineering
J. T. King, Technical Instructor, Civil Engineering
A. J. O'Neill, Technical Instructor, Civil Engineering
R. W. Pratt, Research Engineer, Civil Engineering

Graduate Students:

J. A. Alexander, Research Assistant, Civil Engineering
T. W. Bremner, Research Assistant, Civil Engineering
M. J. Doyle, Research Assistant, Civil Engineering
G. Farra, Research Assistant, Civil Engineering
H. K. Findakly, Research Assistant, Civil Engineering
P. Forootan-Rad, Research Assistant, Civil Engineering
R. C. Laible, Graduate Student, Civil Engineering
A. C. Lemer, Teaching Assistant, Civil Engineering
J. F. Mandell, Graduate Student, Civil Engineering
M. J. Markow, Research Assistant, Civil Engineering
C. R. Nelson, Research Assistant, Civil Engineering
E. F. Olster, Graduate Student, Civil Engineering
J. P. Scott, III, Graduate Student, Civil Engineering
J. E. Soussou, Research Assistant, Civil Engineering
J. N. Sultan, Research Assistant, Civil Engineering

J. L. Walkinshaw, Research Assistant, Civil Engineering

Support Staff:

A. P. Rudolph, Jr., Machinist, Civil Engineering
R. E. Boyd, Administrative Assistant, Civil Engineering
Mary V. Dailey, Language Assistant, Civil Engineering
Maria E. Fleites, Language Assistant, Civil Engineering
Sandra M. Akmentins, Secretary, Civil Engineering
Rosemary H. Driscoll, Secretary, Civil Engineering
Sara Enion, Secretary, Civil Engineering
Lenore Kistler, Secretary, Civil Engineering
Rosa V. Pena, Secretary, Civil Engineering
Marianne N. Stewart, Secretary, Civil Engineering

Degrees Granted:

J. F. Elliott, Ph.D., Civil Engineering, September 1969
G. Farra, S.M., Civil Engineering, February 1969
M. J. Markow, S.M., Civil Engineering, September 1969
C. R. Nelson, Ph.D., Civil Engineering, September 1969
J. P. Scott, III, S.M. and C.E., Civil Engineering, June 1969
J. N. Sultan, Ph.D., Civil Engineering, September 1969

Sponsorship:

Listed under subheadings

Research Report

1.0 Rock Fracture and Tunnelling

1.1 Laser-Assisted Rock Cutting

Personnel: F. J. McGarry, F. Moavenzadeh, P. Forootan-Rad, R. W. Pratt, J. T. King

Sponsorship: United Aircraft Research Laboratories, U.S. Department of Transportation, Office of High Speed Ground Transport, DSR 71551

The purpose of the work reported here is to investigate the effect of lasing on the specific energy and rate of rock removal by mechanical disc cutters. Improvements in either of these quantities may justify laser-assisted tunnelling whether by reducing the energy requirements of rock disintegration or by increasing tunnelling advance rates.

Related Academic Subjects

1.41 Strength of Structural Materials

1.47 Mechanics of Materials

Theses:

G. Farra, "Experimental Observations of Rock Failure due to Laser Radiation," S.M. Thesis, Department of Civil Engineering, February 1969.

C. R. Nelson, "Investigation of Modes of Thermal Fracture of Some Brittle Materials," Ph.D., Department of Civil Engineering, September 1969.

Publications:

F. Moavenzadeh, R. B. Williamson and F. J. McGarry, "Use of Laser and Surface Active Agents for Excavation in Hard Rocks," Paper No. SPE 2240, Proceedings of 43rd Annual Fall

Meeting of the Society of Petroleum Engineers of AIME, Houston, September 29 - October 2, 1968.

G. Farra, C. R. Nelson and F. Moavenzadeh, "Experimental Observations of Rock Failure due to Laser Radiation," Publication R69-16, Civil Engineering, MIT, April 1969.

1.2 Rock Fracture Research

Personnel: F. J. McGarry, F. Moavenzadeh, J. T. King, R. W. Pratt

Sponsorship: U. S. Department of Transportation, Northeast Corridor Transportation Project, C85-65, DSR 76103.

Field studies of the use of surface active agents to assist mechanical tunnelling in hard rock are under study. Advance rates are measured over several hour intervals, in identical rock, with and without the surfactant present in the water used on the tunnel face. The effects of surfactant concentration and water temperature are being studied. Some laboratory investigations are under way.

Related Academic Subjects

1.41 Strength of Structural Materials
1.44 Cementitious Materials
1.46 Portland Cement Concrete
1.47 Mechanics of Materials

Publications:

F. J. McGarry, "Fracture Mechanisms in Natural Rock," Proceedings International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials, Univ. of Southampton, England, April 1969.

F. Moavenzadeh, R. B. Williamson and F. J. McGarry, "Use of Laser

and Surface Active Agents for Excavation in Hard Rocks," Paper No. SPE 2240, Proceedings of 43rd Annual Fall Meeting of the Society of Petroleum Engineers of AIME, Houston, September 29 - October 2, 1968.

G. Farra, C. R. Nelson and F. Moavenzadeh, "Experimental Observations of Rock Failure due to Laser Radiation," Publication R69-16, Civil Engineering, MIT, April 1969.

1.3 Shaped Charge Rock Softening for Continuous Tunnelling Uses

Personnel: F. J. McGarry, F. Moavenzadeh, D. J. Hughes, T. J. Lamb

Sponsorship: E. I. du Pont de Nemours & Co., Inc., DSR 71386

The use of shaped explosive charges with lined cavities can produce jets of the liquefied liner having very high velocities. Upon striking solid surfaces, stagnation pressures of the order of several million psi are achieved. Single cycle applications of this phenomenon, known as the Munroe effect, produce jets capable of penetrating 2 to 10 inches of such materials as steel, concrete, rock and other metals. Theoretical and experimental studies are being performed to evaluate the feasibility of designing and developing a high repetition rate, small charge unit to produce such high velocity jets in quasi continuous fashion for the weakening of hard, strong rock. The unit would be intended for incorporation into continuous tunnelling machines which do not function effectively in hard rock at the present time.

Related Academic Subjects

1.41 Strength of Structural Materials

1.46 Portland Cement Concrete

1.47 Mechanics of Materials

2.0 Concrete and Cementitious Materials

2.1 The Morphology of Hydrated Cements

Personnel: C. B. Arends, S. P. Shah, L. Szekessy, C. B. Doughty

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

Publications:

C. B. Doughty and F. J. McGarry, "Viscoelastic and Elasto-Plastic Analysis of a Fiber Reinforced Composite Material," Publication R68-89, Civil Engineering, MIT, December 1968.

E. Tazawa, R. B. Williamson and F. J. McGarry, "Influence of Curing Time on Shrinkage and Weight Loss of Hydrating Portland Cement," Publication R68-90, Civil Engineering, MIT, December 1968.

L. Szekessy, "Adhesion Between Cement Paste and Aggregate in Concrete," Publication R69-14, Civil Engineering, MIT, March 1969.

F. J. McGarry, A. M. Willner and J. N. Sultan, "Toughening of Glassy Crosslinked Polymers with Elastomeric Inclusions," Publication R69-35, Civil Engineering, M.I.T., July 1, 1969.

2.2 The Relationship Between Microstructure and Mechanical Properties of Cementitious Materials

Personnel: F. J. McGarry, S. P. Shah, T. W. Bremner, P. Forootan-Rad, O. E. Gjorv

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 78898

2.2.1 Studies of Interface

Microscopic and macroscopic studies have shown that the interface between the portland cement matrix and stone particles is weaker than either of the components. As a result, when concrete is stressed, the microcracks which may originate in the matrix go around the particles. It was observed that the introduction of sand and gravel makes concrete more tough and relatively notch-insensitive.

Using X-ray diffraction and the scanning electron microscope, it was observed that a change in microstructure of cement paste occurs at the interface where large crystals of $Ca(OH)_2$ predominate. These crystals may also be the weak points in the cement paste matrix. Ways to reduce the amount of calcium hydroxide was investigated by incorporating siliceous materials which may react with $Ca(OH)_2$.

2.2.2 Studies of Corrosion

One of the major problems with concrete is its deterioration when exposed to aggressive environment such as sea water. An investigation is under way to study the crack initiation and propagation in concrete subjected to sulphate solutions. It is also planned to explore ways of improving concrete's durability by changing its microstructure by the addition of pozzolans or

polymer lattices, or by changing its macrostructure by adding suitable fiber reinforcements.

Related Academic Subjects

1.40 Introduction to Electron Microscopy
1.44 Cementitious Materials
1.46 Portland Cement Concrete

Publications:

E. Tazawa, R. B. Williamson and F. J. McGarry, "Influence of Curing Time on Shrinkage and Weight Loss of Hydrating Portland Cement," Publication R68-90, Civil Engineering, MIT, December 1968.

L. Szekessy, "Adhesion Between Cement Paste and Aggregate in Concrete," Publication R69-14, Civil Engineering, MIT, March 1969.

2.3 Fracture of Brittle Materials

Personnel: F. Moavenzadeh, S. P. Shah, T. W. Bremner, R. Kuguel

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

1.41 Strength of Structural Materials
1.44 Cementitious Materials

1.45 Structural Design of Pavements

1.46 Portland Cement Concrete

Publications:

R. C. Jones and F. Moavenzadeh, "Concrete in the Making," Civil Engineering, Vol. 39, No. 1, January 1969.

F. Moavenzadeh and T. W. Bremner, "Fracture of Portland Cement Concrete," Proceedings, International Conference on Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Southampton, England, John Wiley & Sons, Ltd., 1969.

F. Moavenzadeh and J. Nemec, "Viscoelastic Study of Cement Paste," Proceedings, International Conference on Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Southampton, England, John Wiley & Sons, Ltd., 1969.

R. C. Jones and F. Moavenzadeh, "Trends in Construction Materials: An Overview," Civil Engineering, Vol. 39, No. 8, August 1969.

F. Moavenzadeh and R. Kuguel, "Fracture of Concrete," Journal of Materials, Vol. 4, No. 3, Sept. 1969.

2.4 Ferro-Cement

Personnel: F. Moavenzadeh, S. P. Shah, T. W. Bremner, J. F. Collins, J. S. Claman, H. E. Crow

Sponsorship: Ford Foundation, DSR 76393

The objectives of this study are: a) to investigate the effect of the wire-mortar interface bond on the mode of failure of ferro-cement, and b) to determine the influence of wire reinforcement on the bending strength of square shaped ferro-cement plates.

Related Academic Subjects

1.41 Strength of Structural Materials

1.44 Cementitious Materials

1.46 Portland Cement Concrete

1.472 Composite Materials

Theses:

J. S. Claman, "Bending of Ferro-Cement Plates," N.E. and S.M., Department of Naval Architecture and Marine Engineering, May 1969.

J. F. Collins, "An Investigation into Bond Strength Importance in Ferro-Cement," N.E. and S.M., Department of Naval Architecture and Marine Engineering, May 1969.

H. E. Crow, "Crack Formation, Arrest and Propagation in Concrete Slabs Reinforced with Closely Spaced Steel Wires," S.M., Department of Naval Architecture and Marine Engineering, May 1969.

3.0 Polymers and Composites

3.1 Solidification of Crystalline Polymers

Personnel: F. J. McGarry, C. B. Doughty, J. N. Sultan, M. J. Doyle

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 Academic Subjects

1.40 Introduction to Electron Microscopy
1.44 Cementitious Materials
1.471 Mechanical Behavior of Plastics
1.472 Composite Materials

Publications:

F. J. McGarry and J. N. Sultan, "Crack Phenomena in Crosslinked Glassy Polymers," Proceedings, ASTM National Conference on Composite Materials: Testing and Design, New Orleans, February 1969.

F. J. McGarry and J. N. Sultan, "Crack Propagation in Crosslinked Glassy Polymers," Publication R69-7, Civil Engineering, February 1969.

F. J. McGarry and J. N. Sultan, "The Fracture of Polymers and Fiber Reinforced Polymer Composites," Publication R69-8, Civil Engineering, MIT, February 1969.

3.2 Fibrous Glass Reinforced Plastic Composites

Personnel: F. J. McGarry, J. N. Sultan, R. C. Laible, J. F. Mandell, T. H. Aulenbach, W. E. Schulz

Sponsorship: Dow Chemical Company, DSR 70243; Air Force Systems Engineering Group, Materials Laboratory AF33(615)-2712, DSR 74969.

3.2.1 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 crosslinked resin matrices to prevent microcracking. Micromechanics of toughened resins, molecular flow phenomena. Relationships between microstructure of toughened resins and their resistance to crack propagation.

3.2.2 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

1.41 Strength of Structural Materials
1.42 Structural Materials
1.471 Mechanical Behavior of Plastics
1.472 Composite Materials

Theses:

T. H. Aulenbach, "Plane Strain Crack Toughness of Fiberglass Reinforced Plastic," S.M., Department of Naval Architecture and Marine Engineering, June 1969.

W. E. Schulz, "Fracture Mechanics of Fibrous Composites", N.E. and S.M., Department of Naval Architecture and Marine Engineering, June 1969.

J. N. Sultan, "Criteria in Toughening Thermoset Resins," Ph.D., Department of Civil Engineering, September 1969.

Publications:

C. B. Doughty and F. J. McGarry, "Viscoelastic and Elasto-Plastic

Analysis of a Fiber Reinforced Composite Material," Publication R68-89, Civil Engineering, MIT, December 1968.

F. J. McGarry and J. N. Sultan, "Crack Propagation in Crosslinked Glassy Polymers," Publication R69-7, Civil Engineering, February 1969.

F. J. McGarry and J. N. Sultan, "The Fracture of Polymers and Fiber Reinforced Polymer Composites," Publication R69-8, Civil Engineering, MIT, February 1969.

F. J. McGarry and J. N. Sultan, "Crack Propagation Studies in Crosslinked Glassy Polymers," Proceedings of 24th Annual Conference, Reinforced Plastics/Composites Division, The Society of the Plastics Industry, Inc., Washington, D.C., February 1969.

F. J. McGarry, "Microfracture in Fibrous Glass Reinforced Plastics," Proceedings, Fourth Annual Symposium on High Performance Composites, St. Louis, April 1969.

F. J. McGarry, "Mechanical Behavior of Polymeric-Matrix Composites," Proceedings, ASME/AIAA 10th Structural Dynamics and Materials Conference, New Orleans, April 1969.

F. J. McGarry, "Microcracking in Fibrous Glass Reinforced Resin Composites," Proceedings, International Conference on Structure, Solid Mechanics and Engineering Design in Civil Engineering Materials, University of Southampton, England, April 1969.

F. J. McGarry, A. M. Willner and J. N. Sultan, "Effects of Interstitial Inclusions in Fiber Reinforced Composites," Technical Report AFML-TR-69-86, submitted to Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, May 1969.

F. J. McGarry, A. M. Willner and J. N. Sultan, "Toughening of Glassy Crosslinked Polymers with Elastomeric Inclusions," Publication R69-35, Civil Engineering, MIT, July 1, 1969.

J. N. Sultan and F. J. McGarry, "Microstructural Characteristics of Toughened Thermoset Polymers," Publication R69-59, Civil Engineering, MIT, October 1, 1969.

4.0 Structural Metals and Metallic Composites

4.1 Structural Metals

Personnel: R. C. Jones, F. V. Lawrence, G. F. Doyle

Sponsorship: Inter-American Program in Civil Engineering; Ford Foundation, DSR 76392

4.1.1 Cyclic Loading Effects

Single crystals of alpha-iron have been fatigued in constant stress amplitude reversed plane bending. The S-N curve, the plastic strain amplitude variation, the fatigue induced surface features and the dislocation substructures developed in the crystals during fatigue have been studied.

The formation of a cell structure was shown to occur once a critical dislocation density has accumulated, the nature of which was influenced by the crystallography of the specimen and underwent changes with continued testing. The appearance of the fatigue induced surface features was found to depend upon the nature of the developed substructures. The evolution of a continuous cell structure with testing coincided with a large decline in the level of plastic strain amplitude and it appears that it is these substructures which account for fatigue hardening. From the observations of crack formation and the mode of dislocation movement during saturation, a model for crack initiation is proposed.

4.1.2 Cyclic Frictional Heating of Steel

Samples of material taken from a steel aircraft brake that had been subjected to 260 simulated stops have been examined metallographically. Several different microstructures have been observed and related to the temperatures and cooling rates encountered by the different parts of the brake. Observed macroscopic shrinkage and distortion of the individual brake segments

is explained in terms of superplastic deformation that occurs when the steel austenizes during each stop. Copper from the brake linings is transferred to the steel and causes surface inclusions which increase the wear rate of the brakes by surface fatigue wear.

Unused brake segments were thermally cycled using a focussed CO_2 laser in an attempt to simulate the frictionsl heating in a normal stop. The microstructure of the lased material was different from the microstructures of used brake segments primarily because of the difference in cooling rate.

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:

G. F. Doyle, "The Effect of Cyclic Frictional Heating on the Structure and Properties of a Steel Aircraft Brake," S.M. Department of Metallurgy, January 1969.

Publications:

F. V. Lawrence, Jr. and R. C. Jones, "The Formation of Cell Structures in Fatigued Iron Crystals," Metallurgical Transactions, in press.

4.2 Metallic Composites

Personnel: R. C. Jones, E. F. Olster, K. C. Kvam, D. Laaksonen

Sponsorship: Inter-American Program in Civil Engineering; Ford Foundation, DSR 76392

4.2.1 Joining of Metallic Composites

Joints, approaching 100% efficiency, have been obtained in a 2024 aluminum alloy reinforced with Type 355 stainless steel wires using a deformation diffusion bonding technique. A scarf joint, whose geometry is dependent upon the critical fiber length and the distance between layers of fibers, has been developed in this study.

A wide range of joining parameters (time, temperature, pressure) provided sound joints. The ultimate tensile strength of the joined specimen decreased as bonding times increased, but increased with joining pressure.

The effect of an aluminum oxide coating on the joining surfaces has been investigated and it has been concluded that within the range of bonding parameters used in this study sound joints could be obtained only if the oxide coating was removed immediately prior to joining.

The high strength scarf joint specimens failed with massive debonding along the diffusion bond planes which resulted from the original composite fabrication technique. These fracture surfaces were examined with a scanning electron microscope and appeared nearly identical to fracture surfaces in unjoined, untreated material. The lower strength scarf joint specimens fractured with little or no debonding along these original bond planes.

Preliminary work has been carried out in an attempt to butt joint a composite by exposing reinforcing wires from two members to be joined, overlapping this reinforcement a distance which is a function of the critical fiber length, and finally infiltrating this joint region with molten matrix material. Problems associated with non-uniform infiltration and fiber degradation have not yet been solved.

4.2.2. Fractrography of Metallic Composites

It has been shown that the observed behavior of metal matrix composites can be related to the *in situ* micromechanical behavior of each component, as surveyed at the fracture surface using

scanning electron microscopy. Several metal matrix composite systems, including stainless steel wire reinforced aluminum and boron filament reinforced aluminum, have been studied by such fractrographic techniques.

Diffusion bond planes between the layers of matrix foil employed in fabrication of these composites have been identified as problem areas, particularly in composites containing relatively low volume fractions of reinforcing material. Incomplete bonding at diffusion bond planes has been observed to be a major problem in cross-ply composites. Debonding of diffusion bond planes, observed at fracture surfaces, has been observed on a large scale in both cross-ply and unidirectionally reinforced composites.

Detailed study of matrix metal fracture surface areas permits the observation of microvoids, characteristic of ductile fracture of metals. The number and distribution of these microvoids can be related to the degree of triaxial constraint present in the matrix material, which is affected by matrix-matrix and filament-matrix bonding. Second phase particles in the matrix metal are often associated with these microvoids.

The brittle filaments in the boron-aluminum composite are observed to undergo substantial breakup in the compositing and loading sequence. Possible fracture initiation sites involving brittle filaments can be identified in the fracture surfaces of boron-aluminum composites.

Such scanning electron microscopy observations, made at the fracture surface, can also be related to the gross mechanical properties of metal matrix composites. In situ component behavior at the micro level has been related to such mechanical properties as longitudinal and transverse strengths and stiffnesses of the composites examined.

4.2.3 Irradiation Effects on Metallic Composites

It has been the purpose of this study to examine the effects of nuclear irradiation on the mechanical properties of a metal matrix composite in order to update composite theory to

include nuclear effects and to determine the feasibility of nuclear applications of metal matrix composites.

A 2024-T6 aluminum matrix, NS 355 stainless steel fiber composite was cut into specimens and divided into four sample groups. Three of these groups were irradiated to fast neutron dosages of 1.56, 2.84, and 4.68 x 10^{18} n/cm^2. Microhardness and flexural tests were performed on each of the four sample groups. Fracture surfaces of all sample groups were viewed by scanning electron microscopy.

Strength increases and ductility decreases with increasing dosages were generally observed in the aluminum matrix and the stainless steel fibers. The aluminum hardened a rather large amount and reached saturation at the highest fast dosage. Overall composite strength, as determined by flexural tests, initially decreased, then increased as saturation was achieved in the matrix hardness. The high degree of matrix hardening and subsequent saturation with increasing dosage, leading to changes in the relative failure strain of matrix and fiber, was identified as the controlling mechanism of the composite strength changes in flexure. Diffusion bonding of matrix-matrix and matrix-fiber surfaces was apparently unaffected by nuclear irradiation.

Existing composite theory was concluded to be applicable to nuclear irradiated composites without modification. Nuclear applications were concluded to be most feasible in fast reactors where the "tailorability" of a metal matrix composite might provide the technical breakthrough needed to combat the severe materials problems inherent to fast reactors. The use of nuclear irradiation in micromechanics studies of composites was also concluded a feasible concept.

4.2.4 Corrosion of Metallic Composites

Corrosion studies, with various metal matrix composites subjected to marine environments, have been undertaken in order to evaluate the potential of such materials for use in such hostile environments. Exposure has been to actual and articifial

sea water environments. Weight changes and analysis of solutions after exposure are being employed to determine gross corrosion effects. Detailed microscopic examination, including scanning electron microscopy, has been made to determine corrosion mechanisms in reinforcement and matrix materials.

4.2.5 Fracture Mechanics of Metallic Composites

Fundamental studies at the micromechanism level in metal matrix composites are being employed to develop fuller understanding of behavior under load at the macroscopic level. Experimental and analytical techniques are being employed to study the *in situ* properties of reinforcement and matrix metal, to describe and interpret the mechanisms by which stress is distributed in such composite systems, and to study their fracture initiation and propagation characteristics.

Previous basic research on diffusion bonding of aluminum alloys has been applied to the fabrication of a unidirectionally reinforced metal matrix composite intended for crack propagation testing. Aluminum to aluminum bonds of sufficient strength can be reproducibly fabricated. Fiber to matrix bonding in the stainless steel-aluminum system has not been sufficiently developed to date, however. Experiments with controlled metallurgical interaction between fiber and matrix as a result of additional thermal treatment have been carried out. Control of the mechanical properties of the fiber-matrix interface is required in order to provide a meaningful experimental material with which crack propagation in metal matrix composites can be studied.

An experimental investigation designed to develop a qualitative and quantitative understanding of some fundamental processes governing the fracture of composite materials is being pursued. It is specifically being directed toward describing conditions under which a crack will grow in a stable manner, when a critical crack length is reached, what the failure stress will be in a material having a crack larger than critical size, what conditions govern failure in a crack propagation mode, and

what factors control the notch toughness of a composite.

Related Academic Subjects

1.40 Introduction to Electron Microscopy
1.41 Strength of Structural Materials
1.42 Structural Materials
1.43 Structural Properties of Metals
1.472 Composite Materials

Theses:

E. F. Olster, "Joining of a Metal Matrix Composite," C.E., Department of Civil Engineering, MIT, June 1969.

Publications:

R. C. Jones, "Fractography of Aluminum-Boron Composites," Publication P69-3, Civil Engineering, MIT, June 1969.

E. F. Olster and R. C. Jones, "Joining of a Metal Matrix Composite," Publication R69-25, Civil Engineering, MIT, June 1969.

5.0 Mechanics of Materials

5.1 Viscoelastic Characterization of Engineering Materials

Personnel: F. Moavenzadeh, M. H. Gradowczyk, J. E. Soussou, J. F. Elliott, J. P. Scott, III.

Sponsorship: Ford Foundation, DSR 76393

The objective of this research is to develop constitutive equations for linear and nonlinear time-dependent materials with memory. This will be achieved using (a) multiple-step loading inputs, and (b) random loading inputs. Laboratory experimental results will be used to verify the applicability of these concepts

to various nonmetallic materials. In a later part of the work, the solution of boundary value problems of the theory of nonlinear viscoelasticity will be attempted by using the constitutive equations as derived by the methods described above.

Related Academic Subjects

1.47 Mechanics of Materials
1.471 Mechanical Behavior of Plastics
1.473 Viscoelasticity

Theses:

J. F. Elliott, "Distress and Failure of Pavement Structures," Ph.D., Civil Engineering, MIT, September 1969.

J. P. Scott, III, "Viscoelastic Characterization of Rubber Additive Asphalt," S.M. and C.E., Civil Engineering, MIT, June 1969.

Publications:

J. E. Ashton and F. Moavenzadeh, "Analysis of Three-Layer Viscoelastic Half-Space," Journal of Engineering Mechanics Division, ASCE, Vol. 94, No. EM6, December 1968.

F. Moavenzadeh and J. E. Soussou, "Viscoelastic Constitutive Equations for Sand-Asphalt Mixtures," Highway Research Record, No. 256, February 1969.

F. Moavenzadeh and J. Nemec, "Viscoelastic Study of Cement Paste," Proceedings, International Conference on Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Southampton, England, John Wiley & Sons, Ltd., 1969.

M. H. Gradowczyk, F. Moavenzadeh and J. E. Soussou, "Characterization of Linear Viscoelastic Materials Tested in Creep and Relaxation," Journal of Applied Physics, Vol. 40,March 1969.

M. H. Gradowczyk and F. Moavenzadeh, "Characterization of Linear Viscoelastic Materials, Transactions of the Society of Rheology, Vol. 13, Issue, Interscience Publishers, 1969.

5.2 Viscoelastic Stress Analysis

Personnel: F. Moavenzadeh, J. F. Elliott, J. E. Soussou, M. H. Gradowczyk

Sponsorship: U.S. Department of Transportation, Federal Highway Administration, Bureau of Public Roads, DSR 71183

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
1.473 Viscoelasticity

Publications:

F. Moavenzadeh and J. E. Ashton, "Stresses and Displacements in Linear Viscoelastic Bcdies," Recent Advances in Engineering Science, Vol. III, Gordon and Breach Science Publishers Ltd., London, 1968.

M. H. Gradowczyk, "Numerical Methods in Shell Theory," Publication R68-74, Civil Engineering, MIT, September 1968.

J. E. Ashton and F. Moavenzadeh, "Analysis of Three-Layer Viscoelastic Half-Space, Journal of Engineering Mechanics Division, ASCE, Vol. 94, No. EM6, December 1968.

M. H. Gradowczyk, F. Moavenzadeh and J. E. Soussou, "Characterization of Linear Viscoelastic Materials Tested in Creep and Relaxation," Jnl. of Applied Physics, Vol. 40, March 1969.

M. H. Gradowczyk and F. Moavenzadeh, "Characterization of Linear Viscoelastic Materials, Transactions of the Society of Rheology, Vol. 13, Issue 2, Interscience Publishers, 1969.

J. F. Elliott and F. Moavenzadeh, "Moving Load on a Viscoelastic Layered System - Phase II", Publication R69-64, Civil Engineering, MIT, September 1969.

6.0 Materials in Urban Environment

6.1 Role of Materials in Systems of Constructed Facilities

Personnel: F. Moavenzadeh, J. A. Alexander, A. C. Lemer

Sponsorship: Sloan Basic Research Fund, DSR 27621

The purpose of this study is to identify and to quantify, through a systems analysis approach, the role of engineering materials in urban facilities such as highways. The study will primarily concern itself with determining the extent of change which may be brought about in constructed facilities by (1) change in and control of quality of materials, (2) introduction of new materials, (3) improvement and/or innovation in production, handling, installing, and finishing of materials. The direct and indirect impact of such changes on the constructed facilities will be considered as a measure of need for future research.

Related Academic Subjects

1.41 Strength of Structural Materials
1.42 Structural Materials
1.47 Mechanics of Materials

Publications:

R. C. Jones and F. Moavenzadeh, "Trends in Construction Materials: An Overview", Civil Engineering, Vol. 39, No. 8, August 1969.

A. C. Lemer and F. Moavenzadeh, "The Analysis of Highway Pavement Systems," Publication P69-12, Civil Engineering, MIT, September 1969.

6.2 Maintainability of Systems of Constructed Facilities

Personnel: F. Moavenzadeh, J. A. Alexander, M. J. Markow

Sponsorship: Ford Foundation, Urban Systems Laboratory, DSR 70857

The purpose of this project is to develop a highway maintenance cost model and (computer program) which, for a given road design, location, and use, will predict the total road maintenance costs over a specified period of analysis. Prediction of these costs will enable the engineer to consider more rationally the influence of future maintenance costs in the highway design and maintenance process. Specifically, three distinct steps are proposed for this study:

(1) A review of the available literature in the fields of highway maintenance requirements and standards.

(2) Formulation of a tentative model framework in which the number and types of submodels are specified, relevant variables identified, and the model logic developed.

(3) Calibration of the model and tests of its validity through analyses of field data.

Related Academic Subjects

1.45 Structural Design of Pavements
1.46 Portland Cement Concrete

Theses:

M. J. Markow, "A Systems Analysis of an Urban Transportation Problem," S.M., Department of Civil Engineering, September 1969.

IX. SURFACE PROPERTIES AND BEHAVIOR OF MATERIALS
DEPARTMENT OF MECHANICAL ENGINEERING - SURFACE LABORATORY

Faculty:

B. G. Rightmire, Professor, Mechanical Engineering

E. Rabinowicz, Professor, Mechanical Engineering

W. D. Syniuta, Assistant Professor, Mechanical Engineering

Research Staff:

Dr. J. M. Georges, Visiting Engineer

Graduate Students:

C. Corrow, Research Assistant, Mechanical Engineering

G. J. Buffleben, Mechanical Engineering

J. Kirk, Research Assistant, Mechanical Engineering

Support Staff:

Patricia Howard, Secretary, Mechanical Engineering

Degrees Granted:

C. Corrow, S.M., Mechanical Engineering, January 1969

G. J. Buffleben, S.M., Mechanical Engineering, June 1969

T. J. Bak, S.B., Mechanical Engineering, June 1969

K. L. Zwick, S.B., Mechanical Engineering, June 1969

Sponsorship:

Pratt and Whitney Division of United Aircraft, DSR 71361

The Norton Company, DSR 71338

Sloan Basic Research Fund

1.0 Behavior Under Mechanical Stress of Adsorbed Layers on Tungsten Wire

Personnel: 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. Identical, electro-polished tungsten wires are crossed and loaded normal to the apparent Hertzian contact area. The test liquid is allowed to drip steadily on the crossing of the wires, and a slow, oscillatory, relative sliding motion is imposed on them, so that conditions of equilibrium adsorption may be approximated at each end of a stroke.

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 electropolished surfaces good agreement is obtained. The test surfaces are, therefore, being examined by several methods, to get information 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.

Thesis:

T. J. Bak, "Electron Photomicrography of Electropolished Surfaces," Bachelor of Science, Department of Mechanical Engineering, June 1969.

Publication:

B. G. Rightmire, "Breakdown of Lubrication by Physisorbed Molecules," published in Surface Mechanics, a collection of papers presented at a symposium in Los Angeles, November 1969, American Society of Mechanical Engineers, New York, New York, 1969.

2.0 Fundamental Bearing and Seal Research

Personnel: E. Rabinowicz, W. D. Syniuta; C. Corrow, G. J. Buffleben,

H. Charney

Sponsorship: Pratt and Whitney Division of United Aircraft, DSR 71361

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: W. D. Syniuta, J. Kirk

Sponsorship: The Norton Company, DSR 71338

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 percentage of bonding material) exhibit larger wear flat areas. The wear flat areas also appear

to be directly related to the grinding forces.

Theses:

C. J. Corrow, "Scanning Electron Microscope Fractography Studies of Rolling Contact Fatigue," Masters of Science, Department of Mechanical Engineering, January 1969.

G. J. Buffleben, "Spinning Friction in Thrust Ball Bearings," Masters of Science, Department of Mechanical Engineering, June 1969.

K. L. Zwick, "Electric Discharge Machining of Glass," Bachelor of Science, Department of Mechanical Engineering, June 1969.

X. SURFACE PROPERTIES AND PROCESSES

Faculty:

R. E. Stickney, Associate Professor, Mechanical Engineering

Research Staff:

T. J. Lee, DSR Staff, Research Laboratory of Electronics

D. L. Fehrs, Research Affiliate, Research Laboratory of Electronics

Graduate Students:

J. C. Batty, Graduate Student, Mechanical Engineering

A. Dabiri, Research Assistant, Mechanical Engineering

L. J. Forney, Graduate Student, Mechanical Engineering

H. C. Juvkam-Wold, Graduate Student, Mechanical Engineering

T. Krivachy, Research Assistant, Mechanical Engineering

D. S. Shupe, Graduate Student, Mechanical Engineering

T. Viswanathan, Teaching Assistant, Mechanical Engineering

F. J. Walker, Jr., Graduate Student, Mechanical Engineering

S. Yamamoto, Research Assistant, Mechanical Engineering

Support Staff:

Rose S. Hurvitz, Secretary, Mechanical Engineering

Personnel who have left:

J. C. Batty (Now at Utah State University, Logan, Utah)

D. L. Fehrs (Now at NASA, Cambridge, Massachusetts)

H. C. Juvkam-Wold (Now at Gulf R & D Laboratory, Pittsburgh, Pa.)

T. J. Lee (Now at The Astrophysics Unit, Culham Laboratory, England)

D. S. Shupe (Now at University of Cincinnati, Cincinnati, Ohio)

T. Viswanathan (Now at Cincinnati Milling Machine Company, Ohio)

F. J. Walker, Jr. (Now at Pratt & Whitney, W. Palm Beach, Florida)

S. Yamamoto (Now at Hitachi, Ltd., Tokyo, Japan)

Degrees Granted:

J. C. Batty, Sc.D., Mechanical Engineering, May 1969

A. Dabiri, S.M., Mechanical Engineering, February 1969

H. C. Juvkam-Wold, Sc.D., Mechanical Engineering, May 1969

D. S. Shupe, Sc.D., Mechanical Engineering, January 1969

T. Viswanathan, Sc.D., Mechanical Engineering, May 1969

F. J. Walker, Jr., S.M., Mechanical Engineering, January 1969

S. Yamamoto, Ph.D., Mechanical Engineering, August 1969

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 71627

Cabot Solar Energy Fund, DSR 27541

Joint Services Electronics Program, DA36-039-AMC-03200(E), DSR 70050

National Aeronautics and Space Administration, NGR-22-009-091, DSR 76127

Research Report

The general purpose of our research program is to study problems relating to the atomic, molecular, and electronic processes occurring at gas-solid interfaces. Examples of these processes are: thermionic emission, surface ionization, adsorption, absorption, oxidation, catalysis by metals, 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 solid surfaces. Our major effort has been directed toward obtaining experimental data on both the energy and dipole moment of the adsorption bond between the adsorbate and the substrate. The energy is determined from residence-time measurements based on a modulated molecular-beam technique, whereas the dipole moment is inferred from thermionic and contact-potential measurements of the change in work function during adsorption. To obtain surfaces that are both clean and well-defined, single-crystal specimens are employed together with ultrahigh vacuum techniques. During the past year we have studied the adsorption of various alkali metals, halogens, and oxygen on tungsten. This work will be extended during the coming year, and we also plan to construct an apparatus for detecting surface impurities by Auger electron spectroscopy.

2.0 Oxidation of Metals at High Temperature and Low Pressure

A quasi-thermodynamic approach has been applied to the reaction of gaseous O_2 with various solids (W, Mo, and C) at high temperature and low pressure where the reaction products (oxides) are volatile. Considering the simplicity of the approach, the calculated evaporation rates of the various volatile products agree surprisingly well with existing mass-spectrometric data on these reactions, especially when we account for the fact that not all of the impinging molecules are equilibrated to the surface. Recently we have computed the rate of "erosion" of tungsten by volatile oxidation, and the results provide a semi-quantitative explanation of experimental data.

3.0 Catalytic Reactions at Gas-Solid Interfaces

The abovementioned quasi-thermodynamic approach to heterogeneous reactions has also been applied to catalytic reactions relevant to the control of air pollution. We have considered reactions involving NO, CO, CO_2, N_2, and O_2. The results of these computations were compared with existing data obtained with various catalytic materials. In the future we plan to utilize molecular-beam and mass-spectrometric techniques to determine the kinetics of these reactions and others (e.g., hydrogen dissociation and ammonia decomposition) for several different single-crystal catalysts.

4.0 Scattering of Gas Atoms and Molecules from Solid Surfaces

A modulated molecular-beam apparatus has been used to investigate the collisions of gas atoms and molecules with solid surfaces. The principal goal is to determine the dependence of energy and momentum transfer on the properties of the gas and the solid, and on the structure and composition of the surface. Data have been obtained for the scattering of rare gases and atmospheric gases from the (110) face of a tungsten crystal. The W(110) surface was intentionally contaminated with O_2 and with CO for the purpose of determining the sensitivity of the scattering pattern to the degree of surface contamination. These results illustrate the potential usefulness of low-energy molecular scattering (LEMS) as a technique for studying both the properties of solid surfaces and the dynamics of gas-solid collisions.

5.0 Absorption, Permeation, and Desorption Processes for Gases Dissolved in Metals

We have constructed an experimental apparatus for measuring the spatial and speed distributions of H_2 desorbing from various metals; these data should lead to a better understanding of the process of "activated adsorption." Preliminary measurements are now being performed.

6.0 Electrode Processes in Electrical Discharges

Experimental and analytical studies of the interaction of arcs or sparks with metallic electrodes have been performed, especially for those conditions encountered in electrical discharge machining. The results have led to a clearer understanding of the mechanism responsible for the erosion of material from the electrode surfaces.

Theses:

J. C. Batty, "A Quasi-Equilibrium Treatment of Gas-Solid Interactions," Sc.D., Department of Mechanical Engineering, May 1969.

A. Dabiri, "Transient Desorption of Gases from Metals," S.M., Department of Mechanical Engineering, February 1969.

H. C. Juvkam-Wold, "The Role of Interelectrode Distance in Electrical Discharge Machining," Sc.D., Department of Mechanical Engineering, May 1969.

D. S. Shupe, "Theoretical Analysis of the Effect of Surface Processes on the Permeation of Gases through Metals," Sc.D., Department of Mechanical Engineering, January 1969.

T. Viswanathan, "Erosion Characteristics and Material Transfer in Electrical Discharge Machining," Sc.D., Department of Mechanical Engineering, May 1969.

F. J. Walker, Jr., "Thermionic Studies of Oxygenated Tungsten and Rhenium in a Cesium Atmosphere," S.M., Department of Mechanical Engineering, January 1969.

S. Yamamoto, "Molecular Beam Study of the Scattering of Atoms and Molecules from the (110) Face of Tungsten Crystal," Ph.D., Department of Mechanical Engineering, August 1969.

Publications:

D. S. Shupe and R. E. Stickney, "Thermodynamics of the Solubility and Permeation of Hydrogen in Metals at High Temperature and Low Pressure," to be published in J. Chem. Phys., 1969.

J. C. Batty and R. E. Stickney, "Thermodynamics and Kinetics of Heterogeneous Reactions," M.I.T. Research Laboratory of Electronics, Tech. Report No. 473 (June 1969). (A shortened version of this report has been accepted for publication in the Journal of Chemical Physics.)

D. L. Fehrs and R. E. Stickney, "Contact-Potential Measurements of the Adsorption of I_2, Br_2, and Cl_2 on Bare Cesiated W(100)," to be published in Surface Science.

Y-S. Lou and R. E. Stickney, "Velocity Distribution Measurements for Near-Free Molecule Flow through an Orifice," to be published in the Physics of Fluids.

XI. MOLECULAR BEAM LABORATORY

Faculty:

J. P. Moran, Assistant Professor, Aeronautics and Astronautics
H. Y. Wachman, Professor, Aeronautics and Astronautics
L. Trilling, Professor, Aeronautics and Astronautics

Research Staff:

P. H. Bauer, DSR Staff, Aeronautics and Astronautics

Graduate Students:

Joseph Falcovitz, Research Assistant, Aeronautics and Astronautics
Roy Krupp, Research Assistant, Aeronautics and Astronautics
Leong Ong, Research Assistant, Aeronautics and Astronautics
James C.F. Wang, Research Assistant, Aeronautics and Astronautics
Vreg Yousefian, Research Assistant, Aeronautics and Astronautics

Sponsorship:

Air Force Office of Scientific Research, AF 49 (638)-1601, DSR 76043
National Aeronautics and Space Administration, NGR 22-009-121, DSR 71479
Office of Naval Research, Nonr 3936(03), DSR 79373

Research Report

During the calendar year 1969 our group has consisted of three professors, six graduate students, and one full time research engineer. In addition, several undergraduates have worked in the laboratory and two pre-college youngsters of under privileged background have been employed in the summer as laboratory assistnat.

Our experimental work included the construction, shakedown and preliminary calibration of a large vacuum facility and of a molecular beam source of mixed helium and argon to provide energies up to 2 eV. Design and preliminary testing of instrumentation is now proceeding.

We have worked out a theory for the interaction of ions with solid surfaces in which Auger neutralization occurs on impact. We have completed the new classical interaction model in which a solid is an elastic continuous half space. We have also approached the problem of rarefied flow in nozzles from the continuum and from the kinetic point of view.

Publications:

M. R. Busby and L. Trilling, "The Interaction of Diatomic Gas Molecules with Solid Surfaces", Proceedings of Sixth Rarefied Gas Dynamics Symposium, Academic Press Inc., New York, New York, 1969.

J. P. Moran, H. Y. Wachman, L. Trilling, "Scattering of Monoenergetic Argon Beams from Heated Platinum: Planar Time of Flight Measurements", The Physics of Fluids, vol. 12, no. 5, May 1969.

J. P. Moran, "A Thermal Energy Molecular Beam Source for Use in Scattering Experiments", to be published in Journal of American Institute of Aeronautics and Astronautics.

L. T. Ong, "Thermal Accommodation on Continuum Solid", Master of Science Thesis, Department of Aeronautics and Astronautics, M.I.T., 1969.

M. M. Polak and L. Trilling, "Velocity Distribution Deviations in Molecular Effusion from an Orifice", Proceedings of Sixth Rarefied Gas Dynamics Symposium, Academic Press Inc., New York, New York, 1969.

L. Trilling, J. Falcovitz, J. P. Moran and H. Y. Wachman, "Application of Moleuclar Beams to the Study of Gas Surface Interactions at Low and Moderate Energies", presented by L. Trilling at Second International Symposium on High and Intermediate Energy Molecular Beams, Cannes, France; to be published in Entropie.

J.C.F. Wang and P.H.Bauer, "Measurements of Spatial Distribution of Species in Helium Argon Gas Mixtures Expanding in Supersonic Jets", Proceedings of Sixth Rarefied Gas Dynamics Symposium, Academic Press Inc., New York, New York, 1969.

XII. MOLECULAR BEAM DETECTOR - ADSORBATE SPUTTERING

Faculty:

J. P. Moran, Assistant Professor, Aeronautics and Astronautics

Research Staff:

P. H. Bauer, DSR Staff, Aeronautics and Astronautics

Graduate Students:

L. T. Ong, Research Assistant, Aeronautics and Astronautics

Support Staff:

C. Z. Cox, Secretary, Aeronautics and Astronautics

Sponsorship:

Air Force Office of Scientific Research, AF 49(638)-1601, DSR 76043

Advanced Research Project Agency, SD-90, DSR 71628, DSR 78880

Research Report

We are attempting to detect a molecular beam of neutral argon with translational energies of a few electron volts or larger by the process of collisional sputtering of an alkali metal adsorbed at low coverage on a metal surface. Since the alkali metal is sputtered as ions from a variety of metal surfaces, the process should provide a direct electrical signal proportional to the intensity of the incoming argon beam. In this preliminary investigation, which began in July 1969, we will attempt to detect a sputtered ion signal and relate the detector sensitivity to parameters in the system such as molecular beam energy, alkali metal species and substrate material.

1.0 Adsorbate Sputtering

A coarse theoretical analysis of adsorbate sputtering and a review of available data on bulk phase sputtering by neutral particles leads us to believe that the proposed detection scheme will provide adequate sensitivity to conduct the parametric study mentioned above. The detector is nearly completed and the fabrication of control and detection electronics is underway. A molecular beam source for the production of argon and krypton beams with

translational energies in the range one to six electron volts is being developed under separate contract and should be operational when the sputtering detector is completed.

XIII. CRYOGENIC ENGINEERING LABORATORY
MECHANICAL ENGINEERING DEPARTMENT

Faculty:

J. L. Smith, Jr., Professor, Mechanical Engineering
H. H. Woodson, Professor, Electrical and Mechanical Engineering
C. Kingsley, Jr., Associate Professor, Electrical Engineering
E. G. Cravalho, Assistant Professor, Mechanical Engineering
P. Thullen, Assistant Professor, Mechanical Engineering

Research Staff:

P. A. Rios, Research Associate, Mechanical Engineering

Graduate Students:

K. R. Diller, Research Assistant, Mechanical Engineering
C. Ezekwe, M.I.T. Fellow, Mechanical Engineering
W. S. Harris, Research Assistant, Mechanical Engineering
J. L. Kirtley, Jr., Research Assistant, Electrical Engineering
K. Koenig, Research Assistant, Mechanical Engineering
W. D. Lee, Research Assistant, Mechanical Engineering
D. Luck, Lt., U.S.N., Electrical Engineering
M. Shaw, Research Assistant, Mechanical Engineering
J. F. Sinnamon, Research Assistant, Mechanical Engineering

Supporting Staff:

R. P. Cavileer, DSR Staff, Mechanical Engineering
K. H. Benner, Project Technician, Mechanical Engineering
R. D. Gertsen, Technician A
W. J. Shea, Mechanic
Rachel P. Levin, Administrative Assistant
Susan P. Oliver, Secretary

Personnel who have left:

P. M. Andersen, Research Assistant, Mechanical Engineering (Now at General Electric Co., Lynn, Mass.)
Erica L. Coburn, Research Assistant, Mechanical Engineering (Now at Arthur D. Little Co., Cambridge, Mass.)
R. S. Rosen, Research Assistant, Mechanical Engineering (Now at Sterling School, Craftsbury Common, Vermont)

Personnel who have left (continued):

T. J. Tennison, III, Research Assistant, Mechanical Engineering (Now at Mitre Corp., Bedford, Mass.)

J. O'Callaghan, Machinist, retired.

Degrees Granted:

P. M. Andersen, S.M., Mechanical Engineering, January 1969

Erica L. Coburn, S.M., Mechanical Engineering, September 1969

J. C. Dudley, S. B. and S. M., Mechanical Engineering, May 1969

P. A. Rios y Cartaya, Sc.D., Mechanical Engineering, June 1969

R. S. Rosen, S.B. and S.M., Mechanical Engineering, June 1969

T. J. Tennison, III, S.M., Mechanical Engineering, March 1969

P. Thullen, Ph.D., Mechanical Engineering, May 1969

W. M. Toscano, S.M., Mechanical Engineering, January 1969

Sponsorship:

Partly self-supporting

Union Carbide Grant, DSR 21753

Sloan Basic Foundation, DSR 27687

National Science Foundation (Grant No. GK-3686), DSR 70967

Edison Electric Institute, DSR 71536

Lincoln Laboratory, AF 19(628)-5167, P. O. No. A1681, DSR 71712

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 transient boiling heat transfer to liquid helium for application to the thermal stabilization of superconductors, the engineering problems of refrigeration below 1°K with He^3-He^4 mixtures, the thermal radiation properties of solids at cryogenic temperatures, the propagation of thermal radiation in absorbing media, the freezing and thawing of biological cells.

The research on the application of superconductors to large synchronous generators has continued on an expanded scale. An 85-KVA, 3600 RPM demonstration generator has been completed, run and tested successfully. The generator has a superconducting field winding contained within a rotating dewar vessel. The stator is a room temperature copper winding surrounded by an iron magnetic shield. A 2000 to 6000 KVA generator is being designed and will be constructed within the next two years.

Research Report (continued):

A new project has been initiated to apply the experience of the Laboratory with Stirling cycles to the development of a hot gas engine for power production.

The facilities and services of the Cryogenic Engineering Laboratory have continued to be available to and widely utilized by the Institute Community. Approximately 99,860 liters of liquid helium were supplied in the last year.

Theses:

P. M. Andersen, "Design and Construction of a System for Separation of Mixtures of He^3 and He^4", S.M., Department of Mechanical Engineering, January 1969

E. L. Coburn, "The Effect of a Thin Film on the Radiative Properties of Solids", S.M., Department of Mechanical Engineering, September 1969

J. C. Dudley, "Fabrication of an Armature for a Generator with a Superconducting Rotating Field Winding", S.B. and S.M., Department of Mechanical Engineering, May 1969

P. A. Rios y Cartaya, "An Analytical and Experimental Investigation of the Stirling Cycle", Sc.D., Department of Mechanical Engineering, June 1969

R. S. Rosen, "Infrared Absorptivity of Metals at Cryogenic Temperatures", S.B. and S.M., Department of Mechanical Engineering, June 1969

T. J. Tennison, "Design of a Miniature 20°K Cryogenic Refrigerator Using Welded Metal Bellows Expansion Engines", S.M., Department of Mechanical Engineering, March 1969

P. Thullen, "Analysis of the Application of Superconductivity to Commercial Electric Power Generation", Ph.D., Department of Mechanical Engineering, May 1969

W. M. Toscano, "Radiative Properties of Thermistor Beads", S.M., Department of Mechanical Engineering, January 1969

Publications:

E. B. Qvale and J. L. Smith, Jr., "An Approximate Solution for the Thermal Performance of a Stirling-Engine Regenerator", Trans. ASME, J. Eng. for Power, April 1969, pp 109-112.

P. A. Rios, E. B. Qvale and J. L. Smith, Jr., "An Analysis of the Stirling-Cycle Refrigerator", Advances in Cryogenic Engineering, Vol. 14, 1969, pp 332-342.

Publications (continued):

H. F. Bowman, J. L. Smith, Jr., and T. O. Ziebold, "The Influence of Nuclear Radiation on Pool-Boiling Heat Transfer to Liquid Helium", Trans. ASME, J. Eng. for Industry, Vol. 91, B, 2, May 1969, pp 501-507.

H. F. Bowman, T. O. Ziebold, J. L. Smith, Jr., "Low Temperature Thermal Conductivity of Copper Irradiated with Reactor Neutrons", Thermal Conductivity, Proc. 8th Conf., Edited by C.Y. Ho and R.E. Taylor. Plenum Press, N. Y. 1969, pp 175-184.

E. B. Qvale and J. L. Smith, Jr., "A Simple Correlation for the Heat Transfer Characteristics of a Family of Matrices Subjected to Complex Flow Conditions", Cryogenics, February 1969, pp 62-63.

P. Thullen and J. L. Smith, Jr., "The Design of a Rotating Dewar and Field Winding for a Superconducting Alternator", Paper G-1, presented at 1969 Cryogenic Engineering Conference, June 16-18, U.C.L.A.

L. L. Giventer and J. L. Smith, Jr., "Transient Pool-Boiling of Liquid Nitrogen Due to a Square Wave Heat Flux", Paper I-4, presented at 1969 Cryogenic Engineering Conference, June 16-18, U.C.L.A.

E. G. Cravalho, G. A. Domoto, and C. L. Tien, "Measurements of Thermal Radiation of Solids at Liquid-Helium Temperatures", published in "Thermal Design Principles of Spacecraft and Entry Bodies", Progress in Astronautics and Aeronautics, Vol. 21, Edited by Jerry T. Bevans, Academic Press, New York, 1969, pp 531-542.

E. G. Cravalho and E. L. Coburn, "The Effect of Thin Surface Films on the Radiative Properties of Metal Surfaces", Preprint, Paper No. 69-623, presented at AIAA 4th Thermophysics Conference, June 16-18, San Francisco, California.

XIV. CHEMICAL ENGINEERING OF MATERIALS

1.0 Structure-Property Relationships for Membrane Permeation

Faculty:

E. R. Gilliland, Professor, Chemical Engineering

S. M. Fleming, Instructor, Chemical Engineering

Graduate Students:

S. M. Nemser, NSF Trainee, Chemical Engineering

Sponsorship:

National Science Foundation, GK 1338, DSR 70267

Research Report:

A program for the development of materials for reverse osmosis membranes is being carried out . Membranes are being made from solutions of highly esterified cellulose esters mixed with flux-promoting hydrophilic polymers. Studies have been made with cellulose triacetate (CTA) mixed with either polyethylene glycol (PEG) or polyvinyl-pyrrolidone (PVP). Using 4 weight per cent NaCl, and at a pressure of 1,500 pounds per square inch (psi), the pure homogeneous CTA rejects 99.3 per cent of the salt and has a water flow of only 0.02 gal-mil/square foot/day. Incorporation of either 9 per cent PVP or 9 per cent PEG into CTA membranes increases the water flux by a factor of 5 to 6 with no decrease in salt rejection. Addition of 17 per cent PVP to CTA membranes does not increase the flow over that of 9 per cent addition, but the salt rejection decreases to 80 per cent. On the other hand, addition of 17 per cent PEG increases the flow rate by a factor of 20 over pure CTA membranes, while the rejection drops to only 87 per cent.

The investigation is being continued with PEG and PBP concentrations over a greater range and with other hydrophilic flux-promoting polymers.

A project directed toward fundamental understanding of the structural factors limiting the rates of selective molecular transport through semi-permeable membranes was initiated by Mr. Fleming. Attention has been focused on experimental and theoretical study of the permeation of water and an electrolytic solute (NaCl) through cellulose nitrate membranes. This approach was taken because of the current interest in membrane transport processes, such as reverse osmosis, related to desalination of water.

Cellulose nitrate has excellent salt rejection properties and good chemical stability, but rates of flow of desalted water through the membranes are very low. The question arises as to how the rate of permeation of water through the cellulose nitrate can be promoted,, and if the rate can be increased markedly, what is the effect on the rate of permeation of solutes such as salt?

The approach used thus far has been to cast cellulose nitrate membranes from solution of controlled composition. The organic solvent for the cellulose nitrate is a mixture of a good solvent (acetone or "Ethyl Cellosolve") and a moderately poor solvent (dioxane and/or water). This general technique of preparing membranes is not new, but apparently has not been used successfully in preparation of cellulose nitrate membranes for water desalination.

The initial test results are encouraging; when tested with 1.5N NaCl brine (which is slightly more concentrated in NaCl than sea water) at 1500 psi, 25°C, expanded cellulose nitrate membranes have given 99.5 per cent rejection of NaCl at a water flux of 1.5 gallons per day per square foot of membrane surface. This rejection is adequate to give drinkable water in a single pass through the membrane. The water flux rate is substantially lower than that observed for cellulose acetate under comparable test conditions, and is at least an order of magnitude lower than that required for practical interest. However, it is significant that the product flux through the membrane is two orders of magnitude higher than that through unexpanded cellulose nitrate films, and the intrinsically high rejection of cellulose nitrate films has been retained.

2.0 Reverse Osmosis Desalinization Membranes

Faculty:

A. S. Hoffman, Assoc. Professor, Chemical Engineering
M. Modell, Asst. Professor, Chemical Engineering
S. M. Fleming, Instructor, Chemical Engineering

Graduate Students:

E. Kiran, Undergraduate Student, Chemical Engineering
I. Onal, Undergraduate Student, Chemical Engineering

Sponsorship:

Office of Saline Water, U.S. Dept. of Interior, Grant No. 14-01-0001-1256, DSR 70641

Research Report

Investigation has been completed on the preparation and properties of new membranes prepared by terpolymerizing or tetrapolymerizing various acrylic monomers, in order to develop new and useful reverse osmosis desalination membranes. The membranes are first characterized by their salt and water contents as a function of salt concentration in solution. Following this, their reverse osmosis performance is studied. The results have been interpreted in terms of a model that depicts two water-transport mechanisms: primary H-bonded water free of salt, and secondary water associated with salt ions. From this analysis, predictions have been made as to how composition should be changed to obtain improved flux and permselectivity to water, and these predictions have recently been verified experimentally. In general, the requirements for optimum flux-rejection properties are: a high concentration of hydrophilic sites, randomly distributed in a lightly cross-linked matrix above its glass transition temperature under use conditions. Some of the membranes developed are better in performance (flux and salt rejection) than dense, homogeneous cellulose acetate; work is in progress to polymerize the best monomer compositions in thin layers of porous supports. Sorption isotherms are also being measured for a series of membrane compositions in which the hydrophilic monomer content is progressively increased. Zimm-Lundberg cluster integrals can be calculated from these isotherms and the results are being used to correlate reverse osmosis performance with the distribution of water within the membrane.

3.0 Properties of Complex Coacervates of Polyelectrolytes

Faculty:

A. S. Hoffman, Assoc. Professor, Chemical Engineering

Graduate Students:

S. H. Wu, Scientific Design Fellow, Chemical Engineering

Research Report:

The investigation of viscoelastic behavior of biocolloid-like complex coacervate systems has been completed. Reaction products of oppositely charged polyelectrolytes of different charge frequency along the backbone were studied. The swelling of such materials in salt solutions, such as NaCl, NaBr, and NaI. reveals the increased significance of ion-binding of the halide ion to the quaternary polyion in the series iodide, bromide, and chloride. The salt and water contents of swollen films are measured in

these solutions. Stress-strain behavior of the coacervates immersed in these same salt solutions has led to attempts to correlate and predict the modulus as well as the viscoelastic response based on the swelling data. Measurement of swelling data in these systems also permit a revision and refinement of the equilibrium thermodynamic theory of complex coacervation.

4.0 Catalysis

4.1 Diffusion and Reaction in Porous Materials

Faculty:
C. N. Satterfield, Professor, Chemical Engineering

Graduate Students:
Chon Cheng, Graduate Student, Chemical Engineering
Wayne Pitcher, Graduate Student, Chemical Engineering

Personnel who have left:
J. R. Katzer (Now Assistant Professor, University of Delaware)

Degrees Granted:
J. R. Katzer, Ph.D., Chemical Engineering, October 1969

Sponsorship:
National Science Foundation, GK-1707, DSR 70554

Research Report:

In the recent study of Margetts, the rates of diffusion of methane, normal butane, isobutane, and perfluorobutane into well-characterized single crystals of sodium mordenite were measured at 25 - 100°C, using a rapidly responding constant volume system. The diffusion coefficients were of the order 10^{-8} - 10^{-9} cm^2/sec and exhibited a maximum value with time. Further analysis of Margetts' data shows that this cannot be ascribed to shape, size, or surface irregularities of the crystals if diffusion indeed obeyed Fick's law. Rather, the phenomenon seems to be caused by an initial temperature increase associated with the heat of adsorption. The diffusion charac-

teristics of different samples of mordenite vary greatly and this may be a possible cause of non-reproducibility of catalytic activity.

A paper summarizing the study of Margetts was presented at the Annual Meeting of the AIChE in Washington in November, 1969 and is being submitted for publication in the AIChE Journal.

The recently-completed Sc.D. thesis of Katzer focussed on the counterdiffusion of selected aromatic hydrocarbons in H-mordenite and several type Y zeolites. The pore structure of freshly activated zeolite, in the form of single crystals, was saturated with the hydrocarbon whose diffusion rate was to be determined. The saturated zeolite was then placed in a second aromatic hydrocarbon, and the rate at which the preadsorbed hydrocarbon diffused out was determined.

Benzene and cumene molecules do not counterdiffuse in the pores of H-mordenite. H-mordenite is, however, an active catalyst for the alkylation of benzene to form cumene under the conditions of the diffusion studies, and therefore the reaction must be occurring either on the particle surfaces or just within the pore mouths. Desorption rates of benzene and cumene from H-mordenite are very slow and have associated with them very high activation energies, as high as 20 kcal/mole. For cumene the desorption rate appears to be affected by cumene radical-ions and/or by diisopropyl benzene molecules which are formed by the disproportionation of cumene in the H-mordenite pore structure.

With the type Y zeolites counterdiffusion of benzene, cumene, and even the substituted naphthalenes readily occurs. The rate of desorption is affected by impurities in the hydrocarbons, by the nature of the hydrocarbon into which desorption is occurring, and by the critical diameter of the desorbing molecule; and is much less than the rate of adsorption of the pure hydrocarbon. Activation energies are again very high. The effective diffusion coefficients for 1-methyl naphthalene desorbing from several ion-exchanged forms of the type Y zeolite vary by over two orders of magnitude in the order:

$$NaY < CaY < SK\text{-}500 < CeY < NH_4Y \ .$$

The studies on H-mordenite will be presented in a paper to be given at the Third Joint Meeting of the AIChE and the Puerto Rico Institute of Chemical Engineers, to be held in May, 1970.

The studies on type Y zeolite will be reported at the 2nd International Conference on Molecular Sieve Zeolites to be held at the Worcester Polytechnic Institute in September, 1970 and will be published in a volume in the Advances in Chemistry Series that will contain preprints and proceedings of the conference.

In our current studies, Mr. Cheng is examining various other aspects of the counterdiffusion properties of liquid hydrocarbons in zeolites, including the effects of impurities and some investigation of adsorption equilibria in binary mixtures. Mr. Pitcher is examining restricted diffusion of larger molecules, in the general range of 1000 to 5000 molecular weight, in pores of the order of 20 - 50 Å, such as those encountered in silica gel, Vycor glass, and in a number of industrial catalysts.

Theses:

J. R. Katzer, "Counterdiffusion of Liquid Hydrocarbons in Zeolites," Ph.D., Department of Chemical Engineering, October 1969.

Publications:

C. N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," (book), The MIT Press, 1970.

C. N. Satterfield, A. A. Pelossof, and T. K. Sherwood, "Mass Transfer Limitations in a Trickle-Bed Reactor," A.I.Ch.E. J. 15, 226-234 (1969).

C. N. Satterfield, "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels Above Atmospheric," Correspondence, Ind. Eng. Chem., Fundamentals 8, 175-176 (1969).

4.2 Interphase Electronic Interactions in Polyphase Solid Catalysts

Faculty:

R. F. Baddour, Professor, Chemical Engineering

M. C. Deibert, Asst. Professor, Chemical Engineering

Graduate Students:

R. W. Kline, Research Assistant, Chemical Engineering

Sponsorship:

National Science Foundation, GK-1699X, DSR 70558

Research Report:

Investigation continues on the promoting influence of interphase electronic interaction between the catalyst and the support. The catalyst under investigation is nickel supported on germanium. In this system the magnitude of the Volta potential difference and specific interphase charge transfer can be predicted using the Schottky analysis of metal-semiconductor contact. The variations in these parameters, brought about by changes in the type and concentration of impurities in the germanium, have been shown to influence the kinetics for formic acid decomposition on the supported nickel. Additional measurements are being made to determine if the kinetics of ethylene hydrogenation on the nickel catalyst is similarly influenced by support-catalyst electronic interaction effects. Measurements of total surface area and specific nickel surface area are being utilized to provide a more complete characterization of the nickel-germanium catalyst system. As a part of this research the thermal stability and adsorptive properties of high surface area, vacuum crushed germanium have been determined. Germanium powders with surface areas on the order of 100 square centimeters per gram suffer about 10 per cent loss in area by sintering under vacuum at 300°C for one hour. Neither the freshly crushed nor the sintered germanium powder absorbs measurable quantities of carbon monoxide.

4.3 Heterogeneous Catalysis

Faculty:

R. F. Baddour, Professor, Chemical Engineering
M. Modell, Assistant Professor, Chemical Engineering

Graduate Students:

J. Aleksandrowicz, Graduate Student, Chemical Engineering
J. Apse, Graduate Student, Chemical Engineering
R. Donnelly, Graduate Student, Chemical Engineering
J. Harkness, Graduate Student, Chemical Engineering
K. McNulty, Graduate Student, Chemical Engineering
R. Sills, Graduate Student, Chemical Engineering

Support Staff:

S. R. Mitchell, Project Technician, Chemical Engineering

Sponsorship:

National Science Foundation GK-1699X. DSR 70558

Research Report

One of the long-term objectives of this research is to develop methods for evaluating specific rate constants of elementary catalytic reactions. It is believed that these specific rate constants will be more amenable than overall rate constants to meaningful correlation with parameters of the catalyst. To evaluate specific rate constants, it is necessary and sufficient to know the true sequence of elementary steps (i.e., the mechanism), the rate of the overall reaction, and the concentrations of surface intermediates.

The near-term objectives are to develop techniques for determining mechanisms and concentrations of surface intermediates. To date, efforts have been concentrated on metal-catalyzed, gas-phase reactions.

One method proposed for determining mechanisms and surface concentrations consists of using infrared spectroscopy to measure surface conditions. Surface spectra and overall rate are followed at various temperatures and gas compositions.

Postulated mechanisms are 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 identified by infrared spectroscopy. Palladium-oxygen adsorption bands were not observed because the background absorption of the silica support is intense in the region where Pd-O_2 bands are believed to occur. The results indicated clearly the inadequacy of the conventional kinetic approach for determining mechanisms and the value of simultaneous infrared and kinetic measurements. 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. Two investigations now in progress are aimed at developing methods for obtaining the additional data.

A program was initiated in 1967 with the aim of using this technique for the CO oxidation on silica-support platinum. It was believed that the extinction coefficient for CO adsorbed on Pt would be easier to obtain than that of CO on Pd because the former system exhibits only one infrared band in the 4 to 6μ region whereas the latter system exhibits two. Thus, it had been proposed that only one CO surface species existed on Pt. Quantitative results obtained to data indicate that this interpretation of the Pt-system is too naive. The adsorption isobars and extinction isobars show a maximum in amount adsorbed and adsorbance, respectively. We have tentatively interpreted these data in terms of two adsorbed CO species, each having a C-O stretching band absorbing at the same frequency. More detailed isobars and isotherms are being obtained so that the heat of adsorption of each species can be evaluated. These results indicate clearly the problem associated with basing structural assignments upon observation of a limited region of the infrared. To distinguish between the two species of CO adsorbed on Pt, it will be necessary to determine the normal vibrations of the platinum-carbon bonds which probably absorb in the 10 to 25μ region.

Although H_2 - D_2 exchange on metals (and on nickel in particular) has been the subject of numerous studies, the mechanism is far from understood. Several mechanisms have been proposed, but each is unduly naive because only one form of adsorbed hydrogen is considered to be present (molecular in the Rideal-Eley mechanism, atomic in the Bonhoeffer-Farkas mechanism, etc.). Within the last twenty years, new techniques have been used (e.g., infrared, flash desorption, work function) to show that many adsorbed forms of hydrogen coexist on a given metal, the number of forms increasing with increasing pressure.

The third investigation was initiated in 1968 to determine the mechanism of H_2 - D_2 exchange taking account of the multiple forms of adsorbed hydrogen. The approach once again is to determine simultaneously overall rates and concentrations of individual adsorbed species. Temperature-programmed desorption is to be used to determine surface concentrations of adsorbed species.

The fourth program was initiated in 1968 to bridge the gap between chemisorption and catalytic studies. If the rates of adsorption or desorption of the various species of hydrogen adsorbate and their rates of interchange can be established, then combining this with isotherms for the individual species enables one to predict the rate of H_2 - D_2 equilibration. To maximize chances of success, experiments will be conducted on faces of single crystal nickel under conditions where no more than two or three species are thought to coexist (temperatures above 300°K and pressures below 10^{-5} torr). Much of the desired rate data should be obtainable by electron probe surface mass spectrometry and by flash desorption.

The fifth experiment, initiated in 1968, was directed at studying the rates of an even simpler system. The behavior of CO and NO during chemisorption on a series of clean transition metal films will be investigated. The temperature-programmed desorption technique will be utilized to identify the various species chemisorbing at room temperature and at pressures from 10^{-9} to 10^{-2} torr. The rate of adsorption of the various surface species will be determined by varying the time of adsorption prior to the temperature-programmed desorption. The data will be analyzed in terms of the rate expressions of each of elementary steps involved in the chemisorption-desorption process. It is further

The second investigation was initiated in 1967 to develop general techniques for observing infrared absorption bands of all surface species. The conventional infrared method involves transmissions 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 obscured by the intense absorption of these supports. Thus, metal-oxygen and metal-carbon 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, an attempt is being made to observe reflection spectra of unsupported metals. An interferometer is being used to measure the relatively weak signals. It was estimated that with eighty reflections of the infrared beam between metal foils, it should be possible to quantitatively measure concentrations of surface species down to 5% of a monolayer in the range of 250 to 2500 cm^{-1}. Experiments are in progress for gases adsorbed on palladium foils. The catalysts consists of a bed of fifty 1-mil thick foils separated by 10-mil thick spacers. To date, we have observed various absorption bands which are believed related to adsorbed carbon monoxide and hydrocarbons. The successful development of this technique would significantly enhance the applicability of infrared spectroscopy in catalytic studies and would permit direct observation of phenomena which have been the subject of much speculation and conjecture.

We believe that our efforts to determine mechanisms have been unsuccessful thus far because the reactions we have been studying (CO oxidation on supported Pt and Pd) are more complicated than anticipated initially and presently available techniques are not yet sophisticated enough to handle these complex reactions. We therefore decided to initiate several other programs last year in which we are concentrating on what we hope are simpler reactions. In particular, three more projects have been started; one is concerned with H_2 - D_2 exchange on polycrystalline nickel, a second is concerned with this exchange reaction on each of the three major planes of single crystal nickel, and a third is concerned with the rates of adsorption and desorption of CO and NO on a number of transition metals. Each of these projects is described below.

suggested that infrared spectra of the covered metal surfaces obtained by a multiple-reflection technique will yield information on the structure of the various species chemisorbed. The feasibility of applying such a technique in an experimental system in which temperature-programmed desorption studies can also be carried out will be investigated. The ultimate goal of this project is to increase our understanding of the elementary steps involved in the formation of multiple types of adsorbed species, and to develop correlations of the specific rate constants for the chemisorption processes with parameters of the catalyst.

In an unrelated vein, an exploratory program is in progress concerning the effect of visible and ultraviolet light on gas-phase, metal-catalyzed reactions. In earlier studies, it was demonstrated that light has an appreciable effect on the rate of carbon monoxide oxidation over a palladium catalyst. The effect was attributed to electronic excitation of a surface-adsorbate bond which, in turn, results in a change in the rate of desorption of surface species. The objectives of the present study are to determine the extent to which other systems can be similarly affected, and to investigate more thoroughly the mechanism of the photocatalysis. Monochromatic light of variable frequency will be employed to determine which frequencies are photoactive. The study should provide information on the electronic structure of the bond between the adsorbed molecules and the surface atoms which can be used to interpret and predict the behavior of metal catalysts.

Publications

R. F. Baddour, M. Modell, and U. K. Heusser, "Simultaneous Kinetic and Infrared Spectral Studies of Carbon Monoxide Oxidation on Palladium under Steady-State Conditions," J. Phys. Chem., 72, 3621 (1968).

5.0 Biomaterials

5.1 Non-Thrombogenic Polymers

Faculty:

E. W. Merrill, Professor, Chemical Engineering
K. A. Smith, Associate Professor, Chemical Engineering
E. R. Gilliland, Professor, Chemical Engineering
E. W. Salzman, M. D., Beth Israel Hospital and Harvard Medical School
W. Gerald Austen, M. D., Massachusetts General Hospital and Harvard Medical School

Research Staff:

P. S. Wong, DSR Research Staff, Chemical Engineering
Ellen C. Bellantoni, DSR Research Staff, Chemical Engineering

Graduate Students:

R. E. Gerson, Research Assistant, Chemical Engineering
J. Silliman, Teaching Assistant, Chemical Engineering

Sponsorship:

U. S. Public Health, Contract PH 43-66-491, DSR 76359
National Institutes of Health, Grant HE-08598, DSR 71099

Research Report

Development of non-thrombogenic materials based on heparin bonding via covalent bonds to various polymeric substrates. Materials include hydrogels from polyvinyl alcohol and from gel cellophane, as well as cellulose esters and mixed esters, and the glycidyl mathacrylates.

Applications include dialysis and oxygenation membranes, and implantable prostheses.

Publications:

P.L.S. Wong, E. W. Merrill, and E. W. Salzman, A Non-Thrombogenic Hydrogel Cast From Solution Federation Proceedings 28, 441 (1965)

5.2 Structure and Properties of Elastin

Faculty:

A. S. Hoffman, Assoc. Professor, Chemical Engineering

Graduate Students:

D. Mukherjee, Research Assistant, Chemical Engineering

Sponsorship:

The Medical Foundation

Research Report:

A study has just been completed on the swelling behavior and viscoelastic properties of elastin in various polar organic or aqueous salt solutions. Elastin is a major component of the blood vessels, such as the aorta, and ligaments in the body, and it is hoped that these studies will aid in a better understanding of aging and arteriosclerosis. Elastin behaves as a cros-linked nonpolar rubber, and estimates of the average molecular weight between cross-links (M_c) are obtained from the viscoelastic data. It has been found that purified elastin samples exhibit increased M_c values in a polar organic solvent as formamide, or in mixtures of formamide and water. However, when these solvent systems are exchanged with water and the M_c remeasured in water, there is a marked irreversibility noted for the M_c values of those samples previously in 25 per cent and 50 per cent formamide/water solutions, while the samples previously in 75 per cent and 100 per cent formamide/water solutions display almost complete return of M_c to the lower values noted in water. Aqueous sodium iodide solutions also cause a sharp rise in M_c at as low a concentration as 0.1 per cent NaI (1,000 parts per million), and this effect is irreversible, that is, M_c values remain high even after leaching out the NaI. These results have been interpreted in terms of the molecular structure and arrangment of the polypeptide chains between crosslinks within the elastin matrix. Dr. Carl Franzblau and Marott F. Sinex of the Boston University Medical Research Center, well known for their work on elastin, have been invaluable in their assistance to this project.

6.0 Cryogenic Chemistry

Faculty:

R. C. Reid, Professor, Chemical Engineering

Graduate Students:

G. Rappe, NSF Fellow, Chemical Engineering

Degrees Granted:

G. Rappe, Ph.D., Chemical Engineering, September 1969

Sponsorship:

National Science Foundation, GK-1021, DSR 76384

Research Report:

The research in cryogenic chemistry with emphasis on elucidating the mechanism of reactions between hydrogen atoms and solid olefin films at 77°K has been completed.

In the past year, several important equipment modifications have been effected. Reactions may now be carried out at constanty hydrogen pressure in a sensitive ESR (electron spin resonance) cavity. Hydrogen atoms previously generated by a 2,450 MHz (megahertz) microwave discharge have now, in addition been generated on tungsten filaments heated to temperatures up to 2,200°K. Constant concentrations of hydrogen atoms during the course of the reaction have been obtained and monitored using an electron spin resonance spectrometer.

In this hydrogen atom-lefin gas solid system, in which simultaneous diffusion and chemical reaction occur, experimental variables such as film thickness and hydrogen atom concentration have been studied to assess the relative importance of two competing reaction mechanisms: hydrogen atom penetration and reaction throughout the bulk; and diffusion of olefin and radical species and reaction with hydrogen atoms at the surface. Experimental rates of reaction are in agreement with reaction rates predicted by a "bulk" reaction model.

7.0 Crystal Growth and Nucleation

Faculty:

R. C. Reid, Professor, Chemical Engineering

G. Margolis, Asst. Professor, Chemical Engineering

Graduate Students:

Makoto Ohara, Yoshitomi Pharmiceutical Industries Fellow

J. Tester, Procter and Gamble Fellow

R. Freedman, NSF Fellow

Sponsorship:

National Science Foundation, GK-3696, DSR 71188

Research Report:

Research is under way in two areas of crystallization. In one study, seed crystals of KCl are being grown from aqueous solutions under controlled conditions of temperature supersaturation, and impurity level. The rate of growth of various crystal planes is followed by time-lapse motion pictures taken through a long objective lens microscope. One of the principal results of this study will be to extend the temperature range studied from $0^{o}C$ to almost $100^{o}C$, a much wider range than studied previously. Lead and iron impurities in the parts-per-million range will be added, since preliminary experiments have shown that such impurities exert a profound effect on the rate of growth. Various theoretical models of crystal growth are being formulated to allow a comparison with experimental data.

The second area under study involves the effect of surface morphology and impurities on the rate of vaporization of specific faces of arsenic. Small, well-formed arsenic crystals are heated and vaporized into a vacuum. During vaporization, the macrosurface structure is studied with a microscope. Also, laser reflection patterns are monitored and the rate of evaporation of a given face determined with an interferometer. To accomplish all these measurements, the crystal is set in a furnace on a goniometer and exposed to the various instruments by rotation.

The crystallization research group meets bimonthly with a similar group from Tufts University to discuss new developments in crystal growth kinetics. Various outside speakers are also invited to address the group on such diverse areas as high pressure crystal growth, crystallization from aqueous solutions, and laser reflection techniques.

8.0 Radiation Acceleration of Viscoelastic Processes in Polymers

Faculty:

E. R. Gilliland, Professor, Chemical Engineering

A. S. Hoffman, Assoc. Professor, Chemical Engineering

Graduate Students:

R. Mayer, Research Assistant, Chemical Engineering

Degrees Granted:

R. Mayer, Sc. D. Chemical Engineering, June 1969

Sponsorship:

Atomic Energy Commission Purchase Order from Lawrence Radiation Laboratories, Livermore, Cal., under Contract W-7405-ENG-48, DSR 70049, 74678, 70626

Research Report:

The investigation of the unusual temporary effects of intense radiation fields on the mechanical properties of polymers has been completed. The study of the accelerated creep rate of polystyrene samples in a 3-MeV electron beam resulted in the hypothesis of a mechanism based on temporary accumulation of gases within the polymer during irradiation. Extension of the work to polymethyl methacrylate (PMMA) has led to a revised mechanism, wherein the act of gas generation supplies the necessary energy and local free volume to a particular chain segment. Then, when the radiation is terminated, these gases diffuse to local voids or fissures where they are ineffective in accelerating creep further. This mechanism has been tested with polycarbonate polymer films. It has been found that the critical factor governing the rate of creep during irradiation is the state of strain of the polymer, particularly at higher stresses or higher radiation intensities. At very low stresses or low intensities, the total accumulated dose appears to be the most important factor. A modified Eyring relaxation flow theory correlates most of these data.

SECTION E

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 fields 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. A hybrid water-cooled and superconducting magnet to produce 230 kilogauss is under construction. Further development of this concept is expected to allow the production of continuous fields above 300 kilogauss.

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, multi-photon and non-linear magneto-optical reflection and absorption, cyclotron resonance, magnetic resonance, magnetic susceptibility, magnetoresistance, Mössbauer effect and acoustic absorption. The use of intense laser light sources and ultra low temperature 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:

Professor B. Lax, Director

Dr. D. T. Stevenson, Assistant Director

E. W. L. Davis, Assistant Director for Administration

Research Staff Members:

Dr. R. L. Aggarwal
Professor A. E. Bergles
Dr. C. C. Bradley*
K. J. Button
Dr. C. E. Chase
Dr. D. Cohen
E. J. Cox
Dr. S. Foner
Dr. R. B. Frankel
J. R. Hale
Dr. J. Halpern
Dr. Y. Iwasa
D. Kelland
Dr. D. J. Kim
Dr. H. H. Kolm
M. C. Lavine
M. J. Leupold
Dr. E. Maxwell
E. J. McNiff, Jr.
Dr. R. H. Meservey
Dr. A. Misetich
Dr. D. B. Montgomery
D. R. Nelson
Dr. L. J. Neuringer
Dr. R. R. Oder
A. M. Packard
Dr. C. R. Pidgeon
Dr. H. C. Praddaude
L. G. Rubin
Dr. B. B. Schwartz
Dr. Y. Shapira
F. Smith
Dr. P. M. Tedrow
E. P. Warekois
R. J. Weggel
M. H. Weiler

Visiting Scientists:

Dr. Carlos Abeledo (Brandeis University)
Dr. Fielding Brown (Williams College)
Professor M. Dresselhaus (Professor of Electrical Engineering, MIT)
Dr. G. Faraci (University de Catania)*
S. Fischler (NASA - Electronics Research Center)
Professor G. Landwehr (University of Wurzburg)*
I. De Grave (University of Louvain)*
Professor A. Javan (MIT Physics Department)
Professor S. Legvold (Iowa State University)
Professor M. Lowe (Boston University)
Dr. L. Meyers (Boston University)
Dr. N. Oliveira (University of Sao Paulo)
Professor F. Pollak (Brown University)
Dr. R. Rabitz (MIT Instrumentation Lab)
Dr. H. H. Sample (Tufts University)
Dr. V. N. Schakhtarin (Leningrad Polytechnical Institute)
Professor J. Zak (Technion)*

* Terminated during September 1968 - September 1969

Graduate Students:

Y. Auyang, Graduate Student, Physics (MIT)
D. Abeshouse, Graduate Student, Physics (Boston University)
T. Bernstein, Graduate Assistant, Physics (MIT)
A. Brian, Graduate Student, Physics (Tufts University)
J. M. Cherlow, Graduate Assistant, Physics (MIT)
D. R. Cohn, Graduate Assistant, Physics (MIT)
T. Cronburg, Graduate Assistant, Physics (MIT)
T. Hart, Graduate Assistant, Physics (MIT)
L. Kaufman, Graduate Assistant, Physics (MIT)
N. Lee, Graduate Student, Physics (MIT)
G. Peabody, Graduate Student, Physics (Harvard University)*
U. Smith, Graduate Student, Physics (MIT)
R. Stimets, Graduate Assistant, Physics (MIT)*
J. Tsang, Graduate Assistant, Electrical Engineering (MIT)

Degrees Granted:

H. Goodman, Physics Department, MIT, "Development of an H_2O Gas Laser Employing a Diffraction Grating," B. S. Thesis, June, 1969.

O. M. Dashwood, Physics Department, MIT, "Variation of Magnetization with Temperature in a Sample of Nb-Ti Superconducting Wire," B. S. Thesis, May, 1969.

L. Kaufman, Physics Department, Tufts University, "Quantum Limit Transport Phenomena in Indium Arsenide and Indum Antimonide at Low Temperatures," Ph.D. Thesis, June, 1969.

W. L. Lutts, Jr., Physics Department, MIT, "Methods for Detecting Weak Light Signals," B. S. Thesis, May, 1969.

S. Masmanian, Physics Department, MIT, "The Barnett-Kennard Effect and Geodynamo Theories," B. S. Thesis, June, 1969.

G. Peabody, Physics Department, Harvard University, "Magnetic Flux Penetration in Superconducting Thin Film, Ph.D. Thesis, September, 1969.

A. J. Perlman, Physics Department, MIT, "Low Temperature Thermometry in High Magnetic Fields: Germanium Resistors, Platinum Resistors," B. S. Thesis, May, 1969.

H. W. Polzer, Physics Department, MIT, "Measurements of Energy Released by Flux Jumps in Superconducting Wires," B. S. Thesis, May, 1969.

R. W. Stimets, Physics Department, MIT, "Reflection Studies of Magnetoplasma-optical Phonon Coupling in Polar Semiconductors," Ph.D. Thesis, May, 1969.

FRANCIS BITTER NATIONAL MAGNET LABORATORY
RESEARCH REPORTS

1. High Field Magnet Development

The Laboratory's inventory of 25 high field, water-cooled magnets now covers a sufficiently broad range of diameter, field strength, uniformity and longevity to satisfy the demands of the experimental groups and visitors, at least for the present. This has allowed time for the exploration of new magnet configurations and more extreme conditions of heat flux and stress. Our highest field (225 kilogauss) magnet has been operated with half a dozen versions of inner magnet stack, many of which have exhibited acceptable longevity at heretofore unprecedented levels of either conductor stress or heat flux. All four 150 kG magnets have been field-homogenized to about 1 part in 10^3 over a 1"-diameter sphere, and have even been used for NMR experiments. A 1"-bore magnet constructed with its two stacks in series has generated 170 kG at a power level ($4\frac{1}{2}$ MW) at which its parallel-wound predecessor generated only 159 kG.

Assembly of the hybrid magnet which is designed to generate 225 kG in a 1" bore has been delayed by difficulties, most now remedied, ranging from non-rectangular cross section conductor to excessive nitrogen consumption by the cryostat. The 16"-bore, 26"-O.D. superconducting stack itself, and the parts for the water-cooled insert are complete. A 25 foot, high flow rate, helium transfer tube of novel design to be used to fill the hybrid magnet cryostat has been completed and found to have a very low heat loss.

A long series of studies on the relation of the quench field of superconducting magnets to the properties of short lengths of superconducting wire have borne fruit in the form of a $1\frac{1}{2}$" bore, 80 kG niobium-titanium solenoid. Degraded performance of the solenoid as compared to short samples of the NbTi wire was avoided by using an unwoven polyester fabric interleaving between the layers. The energy released by NbTi during flux jumps has been measured for use with a computer program which predicts the current capacity of composite wires. An experimental technique for predicting coil performance on the basis of short-sample behavior has been employed on wires of many shapes, sizes, and configurations, and indicates the improved stability and AC suitability of multifilament composites twisted axially. Measurements of the high-field current capacity of Tachikawa V_3Ga superconducting composite tapes have indicated performance superior to Nb_3Sn above 150 kG and a small insert coil of V_3Ga ribbon will be built and tested in this field range.

Personnel: D.B. Montgomery, M. Leupold, Y. Iwasa, R. Weggel, N. Pierce (MIT Consul.)

Publications:

JP 330 K. Hechler, G. Horn, G. Otto, E. Saur, "Measurements of Critical Data for Some Type II Superconductors and Comparison with Theory," J. Low Temp. Phys. 1, 27 (1969).

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JP 329 Y. Iwasa, "Magnetization of Single-Core, Multi-Strand and Twisted Multi-Strand Superconducting Composite Wires," Appl. Phys. Lett., Vol. 14, No. 6, 15 March, 1969, pp. 200-201.

JP 357 D. Bruce Montgomery, Solenoid Magnet Design: The Magnetic and Mechanical Aspects of Resistive and Superconducting Systems (Wiley - Interscience, New York, 1969).

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MS 530 D. B. Montgomery, J.E.C. Williams, N. T. Pierce, R. Weggel, and M. J. Leupold, "A High Field Magnet Combining Superconductors with Water-Cooled Conductors," Advances in Cryogenic Engineering, Vol. 14 (Plenum Press, 1969), pp. 88-97.

MS 531 Y. Iwasa and D. B. Montgomery, "Transient Response and Stability Limits of Superconducting Composite Wire Following a Flux Jump," Advances in Cryogenic Engineering, Vol. 14, (Plenum Press, 1969), pp. 114-122.

2.0 Cyclotron Resonance in Semiconductors

2.1 Quantum Effects in Cyclotron Resonance in p-Type Tellurium

The electron cyclotron resonance has been observed as well as a large number of transitions between Landau levels in the valence bands of tellurium. The HCN laser spectrometer was used to study the transitions as a function of temperature. An approximate theoretical model of the valence bands has been selected to calculate the Landau level dependence on magnetic field, identify the observed transitions, calculate the transition probabilities and predict other transitions that can be observed at lower temperatures and higher laser frequencies. The two-fold warping of the valence bands near the forbidden energy gap complicates the theory on the one hand, but also permits the collection of detailed experimental observations of many cyclotron resonance transitions not otherwise allowed.

Personnel: K.J. Button, Margaret Weiler, B. Lax, C.Bradley; P. Grosse, G. Landwehr (University of Wurzburg)

Publications:

JP 305 Benjamin Lax and Kenneth J. Button, "Quantum Magneto-Optics at High Fields," in Physics of Solids In Intense Magnetic Fields, Ed. E. C. Haidemenakis (Plenum Press, New York, 1969) 145-183.

JP 318 Y. Nishina and B. Lax, "Interband Faraday Rotation and Voight Effect in Ge," J. Phys. Chem. Solids 30, 730-747 (March 1969).

MS 494 C. C. Bradley, K. J. Button, B. Lax and L. G. Rubin, "Quantum Effects in Cyclotron Resonance Using a CW Cyanide Laser," J. Quantum Electronics QE-4, 733-737 (1968).

MS 573 B. Lax, "Magneto-optical Properties of Semiconductors," in Proc. IX Internl. Conf. on the Physics of Semiconductors (Nauka, Leningrad, 1968) 253-263.

JP 346 K. J. Button, G. Landwehr, C. C. Bradley, P. Grosse, and B. Lax, "Quantum Effects in Cyclotron Resonance in p-type Tellurium," Phys. Rev. Letters 23, 14 (1969).

JP 358 C. Allen, F. Arams, M. Wang, and C. C. Bradley, "Infrared-to-Millimeter, Broadband, Solid State Bolometer Detectors," Appl. Optics, 5, 813 (1969).

MS 573 B. Lax, "Magneto-Optical Properties of Semiconductors," Proceedings of IX International Conference on the Physics of Semiconductors, Vol. 1 (Nauka, Leningrad), 1968, pp. 253-263.

JP 336 M. H. Weiler, R. W. Bierig, B. Lax, "Photoconductivity Studies of Two-Photon Magnetoabsorption in InSb and PbTe," Phys. Rev. 184, 709 (1969).

JP 377 J. Waldman, D. M. Larsen, P. E. Tannenwald, C. C. Bradley, D. R. Cohn, B. Lax, "Polaron Cyclotron Resonance in CdTe," Phys. Rev. Letters 23, 1033 (1969).

JP 349 R. W. Bierig, M. H. Weiler, B. Lax, "Effects of a Magnetic Field on Optical Mixing Due to Non-parabolicity in n-InSb," Phys. Rev., 186, 747 (1969).

2.2 Polaron in Cadmium Telluride

The interaction of electrons with longitudinal optical phonons in polar semiconductors has been observed in cyclotron resonance at submillimeter wavelengths. This interaction causes the apparent electron effective mass to grow heavier as cyclotron resonance is observed at frequencies nearer to the longitudinal optical phonon frequency. In particular, it was predicted theoretically by Larsen that the Landau levels would be pinned at the longitudinal optical phonon level as the applied magnetic field was increased. Larsen's model was confirmed by observation of several cyclotron resonance transitions using four different laser frequencies and also the Fourier transform spectrometer.

Personnel: D. Cohn, C. Bradley, B. Lax, K. Button; J. Waldman, D. Larsen, P. Tannenwald (Lincoln Laboratory)

2.3 Electron-phonon Interaction in Cadmium Sulfide

Cyclotron resonance of the piezo-polaron has been observed in cadmium sulfide by using the submillimeter molecular gas laser spectrometer. This interaction of the conduction electrons with the acoustical vibration modes of the polar ions of cadmium and sulfur causes the apparent effective mass of the electron to shift toward zero as the acoustical phonons are excited by raising the temperature of the crystal. Simul-

taneously, the cyclotron resonance absorption line of the electron splits with increasing temperature and the several additional branches which appear move rapidly toward larger apparent effective mass. Further study of electron cyclotron resonance with higher frequency lasers will reveal interaction of the electron with other vibrational modes, in particular, the longitudinal optical phonon near a wavelength of 50 micrometers.

Personnel: K. Button, B. Lax, D. Cohn

3. Magnetoplasma-optical Phonon Coupling in Polar Semiconductors

Far infrared reflection spectra of n-type InAs obtained by Fourier transform spectroscopy have been analyzed using the Kramers-Kronig relations to study both frequencies and linewidths of the resonances as a function of magnetic field for three samples of different doping. The data have been compared with theoretical curves calculated from a classical model which includes electron and phonon scattering frequencies as parameters. The experimental dependence of electron scattering frequency on electron concentration has been compared with the theoretical dependence calculated from a Rutherford scattering model for a degenerate electron gas. To fully check our theory, theoretical curves of reflectivity and the imaginary part of the dielectric constant vs. frequency have been calculated and compared with experiment. Overall, the agreement between experiment and theory is quite good.

Personnel: B. Lax, R. Stimets

4. Magneto-optical Studies of Semiconductors Using Modulation Techniques

A detailed study of interband magneto-optical transitions in semiconductors is being made by means of modulation techniques which enable the observation of Landau transitions even at energies far above the band gap. We have applied the stress modulation technique to measure magnetoreflectivity due to the direct transitions at the fundamental edge in germanium, III-V compounds and lead salts. The experimental data for the direct edge in germanium and gallium antimonide have been fitted to the coupled band theory of Pidgeon and Brown used originally for indium antimonide which is a small gap semiconductor. Excellent agreement between theory and experiment was obtained by means of a generalized least squares technique which has provided a very good determination of the conduction and valence band edge parameters for these materials. We have also determined the band parameters for the spin-orbit split-off valence band in germanium, indium antimonide, gallium antimonide, and gallium arsenide from an analysis of the data for the split-off valence to the conduction band transitions. Among the lead salts, we have studied single crystals of bulk lead

telluride. The experimental data on as-grown lead telluride have been successfully interpreted in terms of a Lax two-band model from which we have obtained values for the reduced effective mass and g factor for the conduction and valence band. We have also compared the stress modulated magnetoreflectivity with the wavelength modulated magnetoreflectivity at the fundamental edge in gallium antimonide. The line shapes for the two spectra are very similar which is to be expected if the stress effects on the band structure are considered in the framework of the deformation potential theory.
Personnel: R. Aggarwal, M. Reine, U. Smith

Publications:

MS 491 R. L. Aggarwal, U. Smith, B. Lax, "Magneto-Piezo-Optical-Reflection in Lead Telluride," in Proc. IX Internl. Conf. on the Physics of Semiconductors (Nauka, Leningrad, 1968) 337-341.

JP 307 R. L. Aggarwal, M. D. Zuteck, and B. Lax, "Magnetopiezotransmission Studies of the Indirect Transition in Germanium", Phys. Rev., Vol. 180, No. 3, 15 April 1969, 11. 800-813.

5. Raman Scattering in Solids

Magnon and phonon excitations in opaque insulating and semiconductor materials are being studied by Raman scattering in reflection. The shift in the energy and change in the lifetime of the optical phonon branch of silicon has been measured from 20 to 770°K and correlated with theory. We have measured in α - Al_2O_3 the location of sixteen anharmonic difference frequencies between 24 and 150cm^{-1} which are of importance to the interpretation of ruby fluorescence data. In the antiferromagnet α - Cr_2O_3 measurements of the symmetry and frequency of the optical phonons, the second-order magnon scattering, and the temperature dependence of the first-order scattering from the magnon optical branch up to the Neel temperature have been completed. Two-magnon and phonon scattering in α - Fe_2O_3 and YIG have been observed.

Personnel: R. Aggarwal, T. Hart, B. Lax

6. Optical Properties of Europium Chalcogenides

The fundamental reflectivity spectra of the europium chalcogenides show two strong peaks, E_1 and E_2, at room temperature associated with the corresponding absorption bands. We have studied magnetic ordering effects, as a function of temperature and polarization in a "domain-orienting" magnetic field, on the E_1 and E_2 peaks of the ferromagnetic semiconductors EuO, EuS and EuSe. The results confirm that the peaks are associated with transitions corresponding to the transfer of a localized Eu 4f electron into a very narrow 5d band. Further, they have led to a direct observation of the exchange splitting of the d band at temperatures $\ll T_c$.

We have also carried out high field optical studies of EuTe, which is antiferromagnetic with a Néel temperature $T_N \sim 8°K$. In the ordered state a striking change is observed in the reflectivity as a function of magnetic field as one makes the transitior from antiferromagnetic to parallel ("ferromagnetic") spin alignment. This provides a direct observation of the antiferromagnetic superlattice type of exchange splitting, which has long been proposed theoretically.

Personnel: C. Pidgeon; J. Feinleib, W. Scouler, J. Dimmock, J. Hanns, T. Reed (Lincoln Laboratory)

Publications:

MS 492 C. R. Pidgeon and S. H. Groves, "Electoreflection Study of Inversion Asymmetry and Warping Induced Interband Magneto-optical Transitions in InSb," in Proc. IX Internal. Conf. on the Physics of Semiconductors (Nauka, Leningrad, 1968) 307-312.

MS 503 S. H. Groves, C. R. Pidgeon, A. W. Ewald and R. J. Wagner, "Interband Magnetoreflection of Grey Tin," Proc. IX Internl. Conf. on the Physics of Semiconductors (Nauka, Leningrad, 1968) 43-47.

JP 350 J. Feinleib, W. J. Scouler, J. O. Dimmock, J. Hanus, T. B. Reed, C. R. Pidgwon, "Spin Polarized Splittings in the Temperature Dependent Reflectance of EuO," Phys. Rev. Letters, Vol. 22, No. 25, 23 June, 1969, pp. 1385-1388.

JP 359 C. R. Pidgeon, W. J. Feinleib, J. Scouler, J. Hanus, J. O. Dimmock, T. B. Reed, "Magnetic Ordering Effects on the Reflectivity of EuS and EuSe," Solid State Communications, sched. for Vol. 7/18, 7, 1323 (1969).

JP 366 J. Feinleib, C. R. Pidgeon, "Magneto-Optical Effect of Field-Induced Spin Alignment in Antiferromagnetic EuTe," Phys. Rev. Letters 23, 1391 (15 December 1969).

JP 317 C. R. Pidgeon, S. H. Groves, "Inversion Asymmetry and Warping Induced Interband Magneto-optical Transition in InSb," Phys. Rev., 186, 824 (1969).

7. Two-magnon Absorption in Far Infrared Spectroscopy

We have observed shifts of the two magnon far infrared absorption in MnF_2 on going through the spin flop transition, ~(93kG) for different polarizations of the incident radiation. These shifts are a direct measure of the magnetic dipole-dipole contribution to the spin wave energy at the zone boundary. The observed shifts are in agreement with theoretical predictions based on a rigorous treatment of the dipole-dipole interaction.

Personnel: T. Bernstein, A. Misetich, B. Lax

8. High Field Magnetic Moment and Field Dependent g-Shift in Cerous Magnesium Nitrate

Cerous magnesium nitrate (CMN) is a particularly interesting salt which is used for adiabatic demagnetization in order to achieve ultra-low temperatures and also serves as a low temperature thermometer. Experiments by Williamson and Cape showed that the moment versus field (to 50 kG) deviated slightly from the expected Brillouin function for S = 1/2. In order to examine the magnetic properties of CMN quantitatively, we have made spin resonance experiments over a wide range of fields and observed the g-shifts by means of EPR up to 50 kG in carefully grown CMN crystals. The observed g-shift agrees with theoretical estimates and accounts, within experimental error, for the deviation of the measured magnetization of CMN. In addition we have shown that the g-value of the standard marker, DPPH, changes by less than 0.1% up to fields of 45 kG.

Based on the detailed agreement between theory and experiment for the g-shift in CMN, we have started to examine the magnetic moment versus field in CMN up to 150 kG. The high field data allows a direct and independent evaluation of the temperature independent susceptibility.

Personnel: H. Praddaude, R.F. O'Brien (Weston College), S. Williamson (No. American Rockwell Corp.), S. Foner, E. McNiff, T. Bernstein, D. Cohn

9. Exchange Enhancement of Localized Moments in High Susceptibility Pd Alloys

The magnetic properties of Pd alloys with neighboring elements in the periodic table are being examined in order to determine the effects of band-filling and band structure on the exchange enhancement in Pd and its alloys. Ternary $Pd_{1-x-y}Rh_xAg_y$ alloys have been fabricated in order to examine pseudo-Pd (alloys with an electron concentration of Pd produced by suitable Rh and Ag substitution in Pd). Low field susceptibility as a function of temperature, and high field susceptibilities to 200 kG have been completed. A field dependent susceptibility is detected for sufficiently high susceptibility alloys, as is observed in $Pd_{1-x}Rh_x$ alloys. Although a field dependent susceptibility is observed in the $Pd_{1-x}Rh_x$ alloys when the susceptibility becomes well above that of Pd, there is no apparent field dependence in pure Pd (where detailed band calculations now exist). Exchange enhancements greater than 10 are suggested for some of these materials. Isoelectronic $Pd_{1-a-b}Pt_aNi_b$ alloys have also been examined where the potential scattering from Pt and Ni is expected to be small. It is found that in addition to band-filling effects, scattering effects must be included in order to understand the properties of these alloys.

Various models suggest that the giant moment of Fe in Pd alloys should vary with

the matrix susceptibility, χ_{host}. In addition, the critical Fe concentration, C_{crit}, for the occurrence of ferromagnetism is expected to scale with χ_{host}. Various Pd(Ag, Rh, Pt, Ni, etc.) alloys in the neighborhood of Pd have been examined with dilute quantities of Fe in order to measure the giant moment and C_{crit} versus χ_{host}. No simple relation between the saturated giant moment susceptibility has been observed although the ordering temperature varies linearly with the saturated giant moment of these alloys.

Personnel: S. Foner, R. Guertin (Tufts University), E. McNiff

Publications:

JP 337 S. Foner and E. J. McNiff, "Field-Dependent Magnetic Susceptibility in Exchange Enhanced Pd-Rh Alloys at 200 kG," Phys. Letters 29A, 28-29 (24 March 1969).

MS 526 S. Foner, E. J. McNiff, Jr., "Observations of Field Dependent Susceptibility in Pd(Rh) Alloys at High Magnetic Fields," J. A. P., Vol. 40, No. 3, 1 March 1969, p. 1210.

MS 527 R. Doclo, S. Foner, A. Narath, "Magnetic Susceptibility of Dilute Pd(Rh) and Pd(Ag) Alloys", J.A.P., Vol. 40, No. 3, 1 March, 1969, pp. 1206-1208.

10. Superconducting and Magnetic Properties of High Temperature Superconductors

Measurements of the upper critical field, H_{c2}, as a function of temperature have been made on several new superconducting alloys. The properties of the NbAlGe alloys have been examined to 200 kG in dc fields. The best materials show a value of $H_{c2} \simeq$ 200 kG at 14°K. The highest critical temperature T_c of these materials is 20.7°K. The temperature dependence of H_{c2} suggests that spin-orbit scattering suppresses the Pauli paramagnetic limiting and that the H_{c2} at lower temperatures is well above 200 kG. In addition it appears that practical high-field devices would be feasible in the liquid hydrogen range for these materials if a high current-carrying capacity wire material can be fabricated. The measurements are made with rf techniques which permit examination of the rf loss without electrical contact or further working of the annealed materials. The second class of high temperature superconductors investigated by us is the Nb_3Al system as a function of various metallurgical treatments. Although T_c is lower for these alloys, in contrast with the NbAlGe alloys, single phase materials can be made. Measurements from T_c to 14°K have been completed in a series of these Nb_3Al alloys. Again, it is found that Pauli paramagnetic limiting is almost completely suppressed.

In order to examine Pauli paramagnetism of these alloys directly, measurements of the magnetic moment as a function of field have been made on these high field superconductors above H_{c2}. These are generally consistent with the observed small paramagnetic limiting effects in those alloys.

Personnel: S. Foner, E. McNiff; B. Matthias(Bell Telephone Laboratories and Univer-

sity of California), E. Corenzwit (Bell Telephone Laboratories), T. Geballe Bell Telephone Laboratories and Stanford University), R. Willens and E. Buehler (Bell Telephone Laboratories)

Publications:

MS 524 S. Foner, E. J. McNiff, B. T. Matthias, E. Corenzwit, "Critical Fields of $Nb_3Al_{1-x}Ge_x$ Alloys in Liquid H_2," J. A. P., Aprio, 1969, Vol. 40, No. 5, p. 2010.

JP 339 S. Foner, "Single-Walled, Space-Saving, Liquid Nitrogen Dewars," Rev. of Sci. Instr. 40, 1362 (1969).

MS 533 S. Foner, E. J. McNiff, Jr., B. T. Matthias, and E. Corenzwit, "Properties of High Superconducting Transition Temperature $Nb_3Al_{1-x}Ge_x$ Alloys," in the Proceedings of the 11th International Conference on Low Temperature Physics, St. Andrews, Scotland, pp. 1025-1032.

11. Ultrasonic Measurements in Magnetic Materials

The magnetic phase boundaries are normally examined by means of static magnetic, thermal or specific heat measurements. Ultrasonic attenuation studies have been pursued successfully in a number of magnetic materials. In particular, the ferromagnetic phase transition in EuO has been examined as a function of temperature and field with various modes of propagation of ultrasonic waves.

The phase boundaries of a wide variety of antiferromagnets also have been examined with ultrasonic techniques. Characteristic λ-anomalies are observed for the spin-flop to para-transition up to 200 kG. Materials investigated so far include the classic MnF_2, and FeF_2, αFe_2O_3, $Cr_2O_3 \cdot Al_2O_3$ substitutional systems, and others. The detailed phase boundaries have been examined as a function of temperature and high field for each of these phase boundaries and theoretical analyses based on molecular field approximations have been completed. The ultrasonic techniques provide a unique tool for studying the magnetic phase boundaries of magnetic systems.

Personnel: Y. Shapira

Publications:

MS 441 Y. Shapira, "Giant Quantum Oscillations in the Ultrasonic Absorption;" "Ultrasonic Propagation in High-Field Superconductors," in Physics of Solids in Intense Magnetic Fields, ed. E. D. Haidemenakis (Plenum Press, New York, 1969), 387-389; 378-386.

MS 529 Y. Shapira, T. B. Reed, "Ultrasonic Propagation in EuO", J. A. P., Vol. 40, No. 3, 1 March 1969, pp. 1197-1198.

JP 335 Y. Shapira, "Ultrasonic Behavior Near the Spin-Flop Transitions of Hematite," Phys. Rev. 184, 589 (1969).

JP 347 Y. Shapira, S. Foner, and A. Misetich, "Magnetic Phase Diagram of MnF_2 from Ultrasonic and Differential Magnetization Measurements," Phys. Rev. Letters 23, 308 (1969).

JP 373 Y. Shapira, "Paramagnetic to Antiferromagnetic Phase Boundaries of FeF_2 From Ultrasonic Measurements," Phys. Letters 30A, 388, (1 December 1969).

12. Low Temperature Quantum Limit Transport

A recirculating He^3 refrigerator has been constructed and used to investigate experimentally the galvanomagnetic properties of small gap semiconductors in intense magnetic fields at temperatures below 1°K. The experimental observation of magnetic-field induced carrier freezeout in n-InAs has been used to identify the effects of band tailing in the densities of states. These tails arise from fluctuations in the random distribution of impurity atoms. A consistent interpretation of the data is obtained by postulating that states in the conduction band tail lying below a critical energy do not conduct. In addition, magnetoresistance measurements in the quantum limit have furnished direct experimental evidence of the change in carrier statistics produced by an intense magnetic field.

A He^3 - He^4 dilution refrigerator has been constructed to extend the measurements to very low temperatures below 0.1°K. This apparatus is in the final stages of testing.

Personnel: L. Neuringer; H. Sample (Tufts University); L. Kaufman (MIT Consultant); J. Gerber, A. Brien (Tufts University)

Publications:

MS 498 L. J. Neuringer, "Quantum Limit Transport Phenomena," in Proc. IX Internl. Conf. on the Physics of Semiconductors (Nauka, Leningrad, 1968) 715-720.

JP 345 L. J. Neuringer and Y. Shapira, "Low Temperature Thermometry in High Magnetic Fields: I. Carbon Resistors," Rev. of Sci. Instr. 40, 1314 (1969).

JP 374 L. J. Neuringer, "Magnetic Freeze-Out: The Role of Impurity Density Fluctuations," OAR Research Review, Vol. VIII, No. 6, November-December, 1969 pp. 18-19.

13. High Field Magnetoresistance and the Spin-compensated State in Dilute Alloys

The magnetoresistance has been examined in several dilute alloys including Cu(Fe) and Cu(Mn) (kindly furnished by C. M. Hurd of the National Research Council, Canada and M. D. Daybell and W. E. Steyert of the Los Alamos Laboratories) and in Rh(Fe) (kindly furnished by G. S. Knapp and E. Bucher of the Bell Telephone Laboratories) in the range of 20.4 to 1.3°K. In addition, Cu(Cr) (also furnished by Daybell and Steyert)

has been examined in this temperature range as well. The aims of this study are two-fold; first to examine the suppression of the spin-compensated state at high magnetic fields and second to examine the characteristic behavior of the magnetic impurities and the matrix as a function of field and temperature.

Pulsed field measurements in Cu(Fe) and Rh(Fe) have been extended to 315 kG in order to extend the dc measurements above 200 kG. At 4.2K we find that the spin-compensated state is not completely suppressed. This is consistent with the relatively large Kondo temperatures suggested for these systems.

In order to examine the magnetoresistance in these alloys at lower temperatures a 1-shot He^3 system has been fabricated and measurements have been made in selected dilute alloys.

Personnel: I. DeGrave (University of Louvain), N. Oliveira (University of Sao Paulo)
S. Foner

Publications:

MS 528 I. Degrave, S. Foner, "High Field Magnetoresistance in Dilute Alloys," J. A. P., Vol. 40, No. 3, 1 March 1969, p. 1480.

14. Origin of Ferromagnetism in Alloys of NiCu and NiRh

Renewed interest in the classic NiCu alloys near the critical concentration has been generated by recent neutron diffraction studies which show regions of long-range polarization. This result is quite different from previous models which have suggested a uniform magnetism in this alloy system. Magnetic moment measurement with samples near the critical concentration (kindly furnished by Dr. J. S. Kouvel and Dr. J. Comly of the General Electric Research Laboratories) have been made in order to examine the high field susceptibility and the character of the polarization in these alloys. It is found that the high field susceptibility is relatively independent of Ni content in the region of the critical concentration.

A closely related study of the NiRh alloy system shows similar results in that the high field susceptibility is also relatively independent of the concentration. Comparison with the uniform (Stoner) model shows that the data in NiCu and NiRh are not consistent with this uniform model but rather with a short-range or clustering model.

Studies of the magnetic properties of NiCu alloys with small additions of Fe are being made to examine its effect on the uniform magnetization of these alloys. It is interesting to note that the NiCu(Fe) system is of practical value for desalinization processes. Apparently the Fe inhibits corrosion of NiCu alloys which are used as efficient heat transfer tubes in large scale operations. It has been suggested by Beck, et al. that small amounts of Fe in NiCu series produce appreciable change in the magnetic properties of even dilute NiCu alloys.

Personnel: S. Foner, E. McNiff; E. Bucher (Bell Telephone Laboratories)

Publications:

JP 332 S. Foner, A. J. Freeman, N. A. Blum, R. B. Frankel, E. J. McNiff, Jr. and H. C. Praddaude, "High Field Studies of Band Ferromagnetism in Fe and Ni by Mössbauer and Magnetic Moment Measurements," Phys. Rev. 181, 863 (1969).

15. Magnetic Phase Transitions in Antiferromagnetic Systems

Pulsed field studies of the differential magnetic moment have been made to study the antiferromagnetic to spin-flop and antiferromagnetic to paramagnetic phase transitions in MnF_2. Similar magnetic moment measurements have also been completed on α-Fe_2O_3 both parallel and perpendicular to the c-axis in order to examine the phase boundaries from 4.2°K to the Morin transition. The order of the phase transition is clearly resolved by such measurements.

Personnel: S. Foner, Y. Shapira, A. Misetich

Publications:

JP 304 S. Kurtin, S. Foner and B. Lax, "Ferromagnetic Resonance in Single Crystal $BaO \cdot 6Fe_2O_3$," J. Appl. Phys. 40, 818-821 (February 1969).

16. Studies of Magnetic Properties of Rare Earth Metals and Alloys

The highly anisotropic magnetic properties of RCo_5 compounds where R is a rare-earth atom, e.g. Sm, lead to extremely high energy product permanent magnet alloys. Studies of the magnetic properties in high fields of selected alloys and single crystals of rare-earth metals and alloys permit the evaluation of magnetic behavior of these modern permanent magnet materials. In addition, studies of the magnetic phase transitions in rare earth single crystals are also in progress.

Personnel: S. Foner, R. McNiff, S. Legvold (Iowa State University), J. Rhyne (Naval Ordnance Laboratory)

Publications:

JP 340 S. Foner, Y. Shapira, "Magnetic Phase Transitions in Pure αFe_2O_3" Phys. Lett. A, Vol. 29A, No. 5, 1969, pp. 276-277.

17. Cyclotron Resonance in Graphite

Cyclotron resonance studies in very pure single crystal graphite (these samples were kindly furnished by G. Montet of the Solid State Division, Argonne National Laboratory) have been completed. Additional resonance lines have been resolved which do not fit the known harmonic pattern. These new lines are consistent with detailed theoretical calculations of the conductivity tensor of graphite which include the strong warping of the Fermi surface.

Personnel: H. Praddaude, R. O'Brien (Weston College), D. Nelson

18. Magnetic Properties by the Oscillating Temperature Technique

Detailed studies of the temperature and field dependence of the magnetization of alloys of low concentration iron in palladium were made using the ac temperature technique. Spinwave fits to the magnetization data of 1% iron in palladium, in its ferromagnetic phase, have been reported. For the 1% sample the temperature dependence of the zero field extrapolation of $\partial M/\partial T$ yielded spinwave parameters in good agreement with the results of other magnetic and calorimetric techniques (which are restricted to measurements in zero field). Comparison of $\partial M/\partial T$ measured in a magnetic field with the simple spinwave models used in the zero field comparison, however, yields spinwave parameters which are strong functions of both the temperature and the magnetic field. Unusual behavior of this nature is expected for the strongly exchange enhanced materials but is difficult to study using conventional magnetometry. The $\partial M/\partial T$ technique is uniquely suited to measurement on these systems and is being used to advantage in studies of the departures from ideal behavior observed in these systems.

Personnel: R. Oder, J. Tsang

Publications:

MS 538 R. R. Oder, "$\partial M/\partial T$ Measurements in Ferromagnetic Pd-Fe, J. A. P. Vol. 40, No. 3, 1 March, 1969, pp. 1204-1205.

19. Calorimetric Measurements Employing Oscillating Temperature Technique

The ac temperature technique has been extended to measurements of the temperature and field dependence of the heat capacity, C(T, H) in high magnetic fields. Using this technique we have studied the effect of magnetic fields on critical spin fluctuations in nearly ferromagnetic metals and alloys. In measurements at zero field, we have reproduced the anomalous temperature dependence of the heat capacity

of $Ni_{0.625}Rh_{0.375}$ observed by others and attributed by them to critical spin fluctuations. When measurements were made to 100 kG, however, the anomaly was removed and the heat capacity approximated that of a normal metal over the temperature interval of interest. We have further observed that the suppression of the heat capacity occurred at magnetic fields smaller than that expected from the theory of uniform exchange enhancement commonly applied to these alloys.

In control experiments we have measured C(H, T) for pure indium where we find excellent agreement with accepted values of the heat capacity and of the transition temperature.

Personnel: R. Oder

20. Ultra Low Temperature Studies

The properties of cerium magnesium nitrate in the millidegree region of absolute temperature have been studied by the technique of adiabatic demagnetization. Particular interest has centered about determining the nature of the phase transition which occurs in the neighborhood of 2-3 mK. The evidence of our measurements strongly favors the hypothesis of antiferromagnetism. The transition in cerium magnesium nitrate occurs at a lower temperature than any heretofore observed with the exception of nuclear magnetic transitions. It is of further interest because this substance is widely used as a thermometer in the milli-Kelvin range.

Personnel: E. Maxwell, D. Kelland; G. Zimmerman and D. Abeshouse (Boston University)

Publications:

JP 351 D. J. Abeshouse, G. O. Zimmerman, D. R. Kelland, and E. Maxwell, "Low Temperature Phase Transition in Cerium Magnesium Nitrate," Phys. Rev. Letters 23, 308 (1969).

MS 519 G. O. Zimmerman, D. J. Abeshouse, E. Maxwell, and D. Kelland, "Magnetic Properties of Cerous Magnesium Nitrate in the Millidegree Region," in the Proceedings of the 11th International Conference on Low Temperature Physics, St. Andrews, Scotland, pp. 493-496.

MS 525 J. Zbasnik, L. E. Toth, Y. M. Shy, and E. Maxwell, "Superconducting Critical Fields and Currents of Nb-Ti-N Thin Films in Continuous Magnetic Fields of 175 kG," J. Appl. Phys. 40, 2147 (1969).

21. Mobility of He^4 Ions in Liquid Helium

The mobilities of positive and negative ions in liquid He^4 are being measured between 0.6 and 0.8 K by two methods; time-of-flight and magnetic deflection. The ratio of the two resulting mobilities, which is found to be ≈ 1, yields information about the

interactions involved in the scattering of ions and, in particular, suggests that the dominant scattering is from rotons behaving as point scatterers. Further refinement of the measurements is expected with a new Po^{210} ion source recently acquired. At the same time, development of a new, more sensitive measurement technique is underway. The method, which involves extraction of the ions across the liquid surface and their ultimate detection with an electron multiplier, should increase current-measuring sensitivity by a factor of at least 10^4 over conventional electrometer techniques.

Personnel: C. Chase

Publications:

JP 341 W. Senghaphan, G. O. Zimmerman, C. E. Chase, "Search for Anomalies in the Temperature Dependence of Ultrasonic Velocity in Water," J. of Chem. Phys. 51, 2543 (1969).

MS 518 C. E. Chase, F. Dupre, and M. V. Ricci, "Simultaneous Measurement of Ion Mobility in ^{4}He by the Magnetic-Deflection and Time-of-Flight Methods," in the Proceedings of the 11th International Conference on Low Temperature Physics, St. Andrews, Scotland, pp. 284-286.

MS 520 C. E. Chase and G. O. Zimmerman, "Critical Indices of ^{3}He," in the Proceedings of the 11th International Conference on Low Temperature Physics, St. Andrews, Scotland, pp. 224-230.

22. Properties of Thin Film Superconductors

The critical magnetic field H_c of very thin superconducting aluminum films has been measured as a function of temperature, thickness, and field orientation angle. The temperature ranged from 0.4°K to the transition temperature (near 2°K). The thicknesses were in the range 50 to 200Å. The angular dependence of H_c was determined with an angular resolution of about 0.1. The results show clearly the importance of Pauli paramagnetism for such thin films.

Personnel: P. Tedrow, R. Meservey

Publications:

MS 521 R. Meservey, P. M. Tedrow, "Measurements of the Kinetic Inductance of Superconducting Linear Structures," J. A. P. April, 1969, Vol. 40, No. 5, pp. 2028-2034.

23. Spin and Charge Susceptibility of a Ferromagnetic Electron Gas

The spin and charge susceptibilities of an electron gas in the ferromagnetic state differ significantly from the susceptibilities in the paramagnetic state. Using a Green's function approach we have obtained the diagonal and non-diagonal charge

and spin susceptibility of an electron gas in the ferromagnetic state including the long range effects of the Coulomb potential. Assuming that the effect of an impurity can be represented typically by the addition of both a charge, Ze, and spin, S, interacting with the conduction electrons via an exchange interaction, J (s-d interaction), we have transformed the q-space susceptibility to obtain the spatial response of the up and down spin electrons. Neutron scattering due to magnetic impurities in ferromagnetic Fe for instance has shown qualitatively different spatial spin distributions depending upon whether the impurity is to the right or left of Fe in the periodic table (or equivalently whether one adds or subtracts electrons). Our analysis seems to reproduce the essential features of these neutron scattering experiments.

Personnel: B. Schwartz, D. Kim, H. Praddaude

Publications:

JP 313 B. B. Schwartz and L. W. Grüenberg, "Ultra-High Critical Field in Superconductors with Magnetic Impurities," Phys. Rev. 177, 747-748 (January 1969).

MS 537 D. J. Kim, B. B. Schwartz, "Concentration Dependence of the Range of Spin Polarization in Pd-Fe Alloys," J. A. P. Vol. 40, No. 3, 1 March 1969, pp. 1208-1209.

JP 353 D. J. Kim, H. C. Praddaude, and B. B. Schwartz, "Charge and Spin Susceptibility of a Ferromagnetic Electron Gas," Phys. Rev. Letters 23, 419 (1969).

24. Localized Impurity States in Metals

We have developed a new perturbational approach to the problem of an impurity in a metal based on the Anderson model. Previously we found a logarithmic temperature dependence in the electrical resistance due to the impurity without necessarily having to assume the presence of a localized moment on the impurity. By extending the previous work, we have calculated the temperature dependence of the magnetic susceptibility. In our new results the principal temperature dependence of the susceptibility is logarithmic and this temperature dependence is independent of the Friedel-Anderson-Wolff type criterion for the formation of a local moment.

Personnel: D. Kim

25. Density of States in Palladium

A detailed investigation of the electronic structure of palladium is being performed. Band structure effects have been accounted for utilizing the pseudopotential scheme of Hodges, Ehrenreich and Lang, including the effects of spin-orbit coupling. Using an interpolation scheme we have obtained highly accurate density of states and spin density histograms.

Personnel: A. Misetich; R. Watson (Brookhaven National Laboratory)

Publications:

MS 552 A. A. Misetich, R. E. Watson, "The Susceptibility of Palladium Metal," J. A. P., Vol. 40, No. 3, 1 March, 1969, pp. 1211-1213.

26. Fluorescence From Intrinsic and Extrinsic Excitons in MnF_2

Fluorescence associated with the spin forbidden transition between the $^4T_{1g}$ and the ground state $^6A_{1g}$ has been studied in highly purified MnF_2 crystals containing as few as one part in 10^7 metal impurities. Below 2°K emission from intrinsic excitons accounts for approximately 10% of the total power emitted, the other 90% by excitons bound to noble ions as Mg^{2+} forming "shallow" excitation traps, and to other magnetic ions as Ni^{2+} forming "deep" excitation traps. Intrinsic excitons decay mainly to intrinsic magnon states, while the impurity perturbed excitons decay to impurity magnon states or to the ground state. Simple models for these excitons and magnons permit accurate calculation of the shapes of the magnon sidebands observed in the emission. Time resolved studies show that the impurity excitons are trapped intrinsic excitons, and that the trapping probability is wave-vector dependent.

Personnel: R. E. Dietz, A. E. Meixner, H. J. Guggenheim (Bell Telephone Laboratories, Inc.); A. Misetich

Publications:

JP 347 Y. Shapira, S. Foner, and A. Misetich, "Magnetic Phase Diagram of MnF_2 From Ultrasonic and Differential Magnetization Measurements," Phys. Rev. Letters 23, 98 (1969).

27. Electron Interaction and Electronic Structure in Magnetic Metals and Alloys

By extending Anderson's model for a single impurity in a metal to the case of finite concentration in impurities, the electronic structure and the electron interaction in transition metal alloys are studied. The local environment effect in the impurity magnetization first discussed by Jaccarino and Walker can be reasonably explained by accounting for the local modification of the electronic structure of the hose metal due to the other surrounding impurities. More generally, we have studied the relation between the formation of the localized moment and the occurrence of ferromagnetism as we increase the impurity concentration. Further, by taking into account the modifications of electronic structure and electron interaction due to the presence of impurities simultaneously, various magnetic properties of transition metal alloys are discussed.

Personnel: D. J. Kim

Publications:

JP 314 J. Zak, "Dynamics of Electrons in Solids in External Fields, II," Phys. Rev. 177, 1151-1160 (15 January 1969).

JP 333 W. Zawadzki, "Bloch Electrons in Crossed Electric and Magnetic Fields," in Physics of Solids in Intense Magnetic Fields, ed. E. D. Haidemenakis, (Plenum Press, New York, 1969) 311-328.

JP 334 W. Zawadzki, "Electrons in a Magnetic Field," in Physics of Solids in Intense Magnetic Fields, ed. E. D. Haidemenakis (Plenum Press, New York, 1969) 301-310.

28. Mössbauer Effect Studies

Mössbauer studies of Fe^{2+} in cubic MgO have been completed. Under the influence of a suitable uniaxial stress, the quenching of the electronic angular momentum of the low lying threefold degenerate Γ_{5g} level of Fe^{2+} has been observed. This result can be explained in terms of Ham's random strain model which predicts the appearance of a quadrupole doublet at low temperatures. A value for the strain coefficient of Fe^{2+} in MgO has been obtained: $G_{11} = 585\ cm^{-1}$.

An investigation of the $Mo_{1-x}Nb_x$ system reveals that the monotonic decrease in the average moment on the Fe impurities with increasing x does not result from a continuous decrease in the actual moment, but rather is due to an increasing number of iron sites which discontinuously become non-magnetic. The result is in qualitative agreement with the Jaccarino-Walker model of discontinuous moment formation depending upon the local impurity environment. Studies of the high magnetic field dependence of the hyperfine field of an Fe nucleus in various strongly exchange enhanced alloys such as PdPt, PdNi, PdRh, and NiRh are continuing.

Personnel: R. B. Frankel, A. Misetich; J. Chappert (Grenoble), C. Abeledo (Brandeis), N. Blum (NASA/ERC)

Publications:

JP 328 J. Chappert, R. B. Frankel, A. Misetich, N. A. Blum, "Quadrupole Moment of ^{57}Fe," Phys. Letters 28B, 406-407 (6 January 1969).

JP 310 J. Chappert, R. B. Frankel, A. Misetich, N. A. Blum, "Multiple Charge States, Hyperfine Interactions and Relaxation Processes of Fe in ^{57}Co doped MgO," Phys. Rev., Vol. 179, No. 2, 10 March 1969, pp. 578-589.

JP 332 S. Foner, A. J. Freeman, N. A. Blum, R. B. Frankel, E. J. Mcniff, Jr. and H. C. Praddaude, "High Field Studies of Band Ferromagnetism in Fe and Ni by Mössbauer and Magnetic Moment Measurements," Phys. Rev. 181, 863 (1969).

JP 355 R. B. Frankel, "Hyperfine Interaction in Gd in Diamagnetic, Metallic Hosts," Phys. Letters A, 30A, 269 (1969).

JP 342 R. B. Frankel, Y. Chow, L. Grodzing, J. Wulff, "Nuclear Zeeman Effect in W^{183} in Iron," Phys. Rev., Vol. 186, 381 (1969).

29. Survey of Approximation Techniques for Double Time Thermodynamic Green's Function

Green's function techniques are commonly applied to theoretical analyses of dilute impurity problems in strongly enhanced itinerant electron paramagnetic alloys. These studies bear on the nature of magnetism and local moments in metals and alloys - problems which are being examined with several techniques in the Laboratory. A survey of various analytical approximation techniques has been completed.

Personnel: H. C. Praddaude

30. Cooperative Programs

About half of the magnet operating hours in 1969 were used by visiting scientists who carried out a wide variety of experiments primarily in solid state physics. A group from Brandeis University observed nuclear resonance of the proton at 130 kilogauss, the highest field ever for any NMR experiment. A group from Raytheon made high field magnetization measurements on their new samarium-cobalt permanent magnet alloys. Other experiments by visitors included many on the band structure and conduction properties of semiconductors, semimetals and alloys, Zeeman spectra of rare-earth ions in host crystals and the high field properties of superconductors.

SECTION F

INSTRUMENTATION LABORATORY

The Instrumentation Laboratory, a division of the Department of Aeronautics and Astronautics, is a defense research organization 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

M. S. Sapuppo, Associate Director

Staff Members Participating in Materials Research:

Mrs. L. K. Garfinkle

R. L. Morey

J. L. Nelson

Dr. J. R. Stemniski

P. J. White

R. L. Williams

Sponsorship:

Listed under subheadings

REPORT ON RESEARCH ON MATERIALS AT THE INSTRUMENTATION LABORATORY

1.0 Liquid Lubricants in Vacuum Environments

Personnel: R. Morey
Sponsorship: NASA Contract NAS 9-4065

Research Report

The use of silicone fluids as a lubricant in a vacuum environment is under continuing investigation. The need has arisen for developing a lubricant with better properties for prolonged vacuum exposures and consultation is being made with various organizations to determine the choice of test fluids. Preliminary tests have been carried out but extensive performance tests are to be run.

2.0 Materials in Manned Submersible Environments

Personnel: R. Morey
Sponsorship: Navy Contract N00024-67-C-0207

Research Report:

Various non-metallic materials which are to be used in the guidance system of a manned submersible have been tested to determine their flammability characteristics. Test conditions have included three atmospheres of air and up to 40% oxygen. Combustion rate has been established for such materials.

3.0 Materials in Deep Ocean Environments

Personnel: R. Morey
Sponsorship: W.H.O.I. P.O. #17052

Research Report

A continuing program is being undertaken with Woods Hole Oceanographic

Institution to determine choce of materials for long term exposures. Corrosion prevention schemes such as cathodic control are being investigated. Determination of failure modes of different cable configurations are being carried out and correlation is being made with deep sea failures and in air laboratory tests.

4.0 Investigation of Curing Schedule of Dow 332 Epoxy Resin and BA-1 Activator

Personnel: Dr. J. R. Stemniski, R. L. Williams
Sponsorship: Navy Contract N00030-66-C-0189
NASA Contract NAS 12-569

Research Report:

The degree of cure for long term application of epoxy resins is quite critical. Incomplete cure can result in compatibility problems, as well as deficiencies in mechanical structural properties. Infrared analysis of degrees of cure has proven to be quite satisfactory, as is reported extensively in the literature. Application of the IR technique to Dow 332 epoxy resin and BA-1 activator (piperidine) indicated that a cure schedule can be outlined with reasonable certainty.

While IR gives good evidence that cures are effected, a program utilizing thermogravimetric analysis, differential thermal analysis, and differential scanning calorimetry is presently underway to supplement the IR method for determining accurate cure schedules and stoichiometry of resin-activator systems.

5.0 Conductivity Measurements of Low Viscosity Fluids

Personnel: Dr. J. R. Stemniski, Mrs. L. K. Garfinkle, R. L. Williams
Sponsorship: Air Force Contract AF 04(694)-999
NASA Contract NAS 12-569

Research Report:

A physical property of low viscosity fluorocarbon fluids which is of particular interest is that of conductance. A program which will utilize a differential amplifier technique has begun. The test method involves using a cell having a constant of 0.01 cm^{-1} as a detector and a differential amp-

lifier in the measuring circuit. It is expected that values in the conductance range of less than 4×10^{-9} mho can be obtained from this method.

6.0 Molecular Weight Distribution Determination of Gyro Damping Fluids By The Thermal Diffusion Method

Personnel: Dr. J. R. Stemniski, R. L. Williams
Sponsorship: Navy Contract N00030-66-C-0189

Research Report

The molecular weight distribution of bromotrifluoroethylene fluids is determined using an M. Fink thermal diffusion column. However, it has been demonstrated by Round Robin testing in committee F-7-F of the American Society for Testing and Materials that reproducibility of this test technique is not good. The ASTM committee has postulated many theories as to the lack of reproducibility, but unfortunately exact experimental conditions are not readily available. The Miniature Components Group Materials Laboratory has recently set up a thermal diffusion column and a program is being undertaken to determine which operating parameters most greatly affect the test results. Progress in this area is quite slow, since only one parameter at a time can be varied, and length of the test run (8-10 days) limits the number of experiments that can be performed.

7.0 Properties of Bromotrifluoroethylene Telomer Fluids

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

In order to understand why bromotrifluoroethylene (BTFE) telomer fluids turn yellow when exposed to ultraviolet light, BTFE was treated with several reagents. It has been theorized that the yellow color observed in fluids is due to bromine release, which results in an unsaturated system. These tests were performed to determine if free bromine could be detected and also what chemical reagents can cause a similar phenomenon.

A solution of telomer fluid in methanol when exposed to UV lights turns yellow. However, when oxygen is eliminated, the solution turns clear. Addition of oxygen regenerates the yellow color. The presence of an as

yet unidentified free radical in both solutions has been confirmed by the use of 2, 2-diphenyl-1-picrylhydiazyl. Other tests confirm the evolution of bromine from the yellow solution.

8.0 Low Temperature Effects on Damping Fluids

Personnel: Dr. J. R. Stemniski, R. L. Williams
Sponsorship: LRL Contract AT (30-1)-3911
Navy Contract N00030-66-C-0189

Research Report

Because inertial measuring units are temperature-cycled during qualification testing, it is important to understand the properties of fluids at low temperatures. Various damping fluids and one balancing fluid were subjected to temperature and pressure environments in the 0 to 3 atmosphere range and the -100° to $+200^{\circ}$F temperature range. Most of the fluids tested were in the 2.3+ gm/cm^3 density range, with varying viscosities. Samples tested were outgassed and non-outgassed, thin-section and bulk, with and without temperature probes in contact with the fluid, and at various time rates of change of temperature. In some cases, care was taken to exclude atmospheric gas from a closed system being tested.

In general, it was found that the crack temperature is lowered by:

(1) lower viscosity fluid
(2) outgassing the fluid
(3) rate of cooling

The crack temperature is raised by:

(1) presence of thermocouple probe
(2) shock
(3) increased pressure

The outgassed fluid in a closed container, filled and capped under pressure, cracks at a higher temperature than one which has been only outgassed. Thin-film and narrow cross-section fluids behave much the same as bulk fluid. Cracks cause bubbles even in degassed fluid. The fluid undergoes a phase change at a temperature much higher than the crack point. The pour point was determined as $35^{\circ} \pm 5^{\circ}$F for most fluids. No accurate determination of cloud points could be made since most of the fluids exhibited glass-transition states.

NOTE: This work is a continuation of the preliminary work reported

in Research in Materials, 1968-1969.

9.0 Some Applications of Computer Technology to Gel Permeation Chromatography

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189
NASA Contract NAS 12-569

Research Report:

Gel permeation chromatography (GPC) is a useful tool in determining molecular weight distributions of polymer systems. The data is presented as a recorded curve and is easily obtained. However, interpretation of the GPC chromatogram can be a difficult task. Automatic curve resolvers are available, but are quite expensive and impractical where small numbers of curves are resolved. This program involved the development of a method that takes the best experimental GPC data available for a mixture and mathematically resolves it into a set of curves that corresponds to the components of the original sample. It assumes that all single-component samples will give the same general curve shape, i.e., a Gaussian curve. Therefore, a set of these curves may be added to obtain the GPC chromatogram of a mixture of components. Here the single component curve will be Gaussian, but the method itself may be adapted to other kinds of curves. Since this method is iterative, computer programs written in BASIC are also considred to cut down the time required to resolve a GPC. The computer is assigned the tedious work of calculatiing and plotting, and the operator is left to jedge the output. With this method, a GPC chromatogram can be resolved in about 30 minutes.

10.0 Heat Transfer Analysis of the M. Fink Thermal Diffusion Column

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

The thermal diffusion column used to determine molecular weight distributions of gyro damping fluid has been the subject of considerable analysis since it has been determined that reporducibility is lacking. This

had been determined during a Round Robin testing program conducted by ASTM committee F-7-F. Several possibilities for the lack of correlation had been suggested. It was decided that a mathematical heat transfer analysis be performed on the column. The study revealed that water temperature control, while not the sole contributor to inconsistencies, is a major contributor. The thermal diffusion column can operate in a low temperature difference region or in a high temperature difference region. Also, if the temperature drop across the fluid is low, the convection in that layer is low. A higher temperature drop will cause more convection.

These facts may explain the greater separation of damping fluids at low water flow rates. At low flow rates, just enough convection may occur to segregate the fluid components. At higher flow rates, the higher temperature difference, coupled with the fluid's relatively high density variation with temperature, will cause too much convection in the sample layer. Any tendency to segregate will be counteracted by the greater degree of mixing. This theory will be tested in an experimental program to determine its accuracy.

11.0 Accelerometer Fluids

Personnel: Dr. J. R. Stemniski, Mrs. L. K. Garfinkle, R. L. Williams
Sponsorship: Air Force Contract AF 04(694)-999
NASA Contract NAS 12-569

Research Report:

Third generation specific force integrating receivers have placed an increased density requirement on accelerometer fluids. Densities in the 2.7 gm/cm^3 range are now required for successful operation. The problems associated with obtaining such high densities are mainly concerned with physical and chemical stability. In order to achieve such high densities, it is necessary that the molecules be a single species and essentially heavily laden with large halogen atoms such as bromine.

A promising candidate fluid - tribromofluoromethane - was obtained from the DuPont Company, Organic Chemicals Department. This compound has a very high density of 2.675 gm/cm^3 at 125^oF and a viscosity of 1.11 centipoises at 125^oF. It has performed well in compatibility testing and appears to be the prime candidate for application in new instrument design.

Tribromofluoromethane is sensitive to ultraviolet light and precautions must be taken to avoid long exposure. This is accomplished by using

commercially available UV screening sheets.

Samples of tribromofluoromethane have been obtained from four companies and it appears that alternate sources will be no problem.

Other fluids studied include the following:

Fluid	Source	Density (gm/cm^3 @ 125^oF)	Viscosity (centipoises @ 125^oF)
FC-370	Halocarbon Corp.	2.561	3.53
FC-375	Halocarbon Corp.	2.585	5.03
NC-1851	Dow Chemical	2.356	3.84
NC-1852	Dow Chemical	2.565	12.95

12.0 Bromotrifluoroethylene Telomer Gyro Damping Fluids

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

The presently used gyro damping fluids are generally believed to be telomers of bromotrifluoroethylene. They are unique because they possess both high density and high viscosity while remaining in the fluid state. While these materials have useful properties and are normally quite good, the disadvantage of a single source is ever present. In order to alleviate this problem, the Navy has sponsored a program at Pensinsular ChemResearch designed to duplicate the properties of the fluid used in Navy inertial measuring units.

Peninsular has completed a one-year program in which a fluid possessing a density of 2.403 gm/cm^3 and viscosity of 2600 centipoises has been successfully synthesized. These properties closely match the design specification. However, certain modifications are necessary to reproduce exactly the specified properties. In addition, the fluid meets the other requirements of the specification.

It is expected that a three-month extension of effort will result in an exact duplication fluid. After this is accomplished, a 50-pound production batch will be prepared and submitted for final qualification in inertial measuring units.

The Miniature Components Group Materials Laboratory monitors this program quite closely and conducts analytical investigations on prototype fluids. In this area, gel permeation chromatography has been extremely

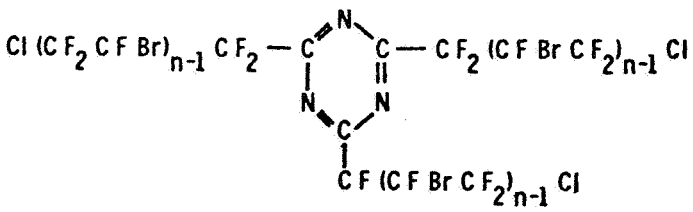
useful in predicting molecular weight distributions of candidate molecularly distilled fractions of fluids.

13.0 Single Species Gyro Damping Fluids

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

Peninsular ChemResearch, Gainesville, Florida, under Navy sponsorship, recently completed a research program directed at synthesizing a singular molecular species fluids. The goal of this effort was to synthesize high density-high viscosity fluids based on the heterocyclic s-triazine system. Properties are determined by the length of the side chains.



Triazine fluids have been prepared, where n = 2, 3, 4, which have exhibited densities of 2.09, 2.21, and 2.32 gm/cm^3 at room temperature. It is expected that when n = 5, a density in the 2.45 gm/cm^3 range will be obtained.

This research effort will be continued at the University of Florida under the direction of Professor Paul Tarrant. The emphasis of the continuation will be placed on preparing triazines where n = 5 and higher.

14.0 Gel Permeation Chromatography

Personnel: Dr. J. R. Stemniski, Mrs. L. K. Garfinkle, R. L. Williams
Sponsorship: Air Force Contract AF 04(694)-999
Navy Contract N00030-66-C-0189
NASA Contract NAS 12-569

Research Report:

The development of the technique of gel permeation chromatography (GPC) for use in analyzing damping fluid mixtures has been reported in previous issues of this communication. The utility of this method is constantly demonstrated in routine quality control work, as well as in research projects. The GPC is continually used in determining molecular weight distributions of damping fluids and epoxy resins. It has proved most useful in directing the research effort of Peninsular ChemResearch, Gainesville, Florida, toward the development of damping fluids.

15.0 Separation of Damping Fluid Mixtures by Liquid Chromatography

Personnel: Dr. J. R. Stemniski
Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

While gel permeation chromatography can separate damping fluid mixtures into its components, this technique is not practical for large scale separation. Waters Associates, Framingham, Mass., is presently separating a large sample (128 grams) into components. This will allow determination of physical properties of individual components and will enable the preparation of a meaningful calibration curve.

16.0 Boron Carbide Surface Studies

Personnel: J. L. Nelson, P. J. White
Sponsorship: NASA Contract NAS 12-569
Air Force Contract AF 04(694)-999

Research Report:

A method of final finishing the critical surfaces of boron carbide (B_4C) gas bearing parts has resulted in surfaces of superior fineness which also achieve the critical geometry. The technique is one of high-speed polishing or lapping of the boron carbide part with a suitably designed tool or plate of the same material. No lubricant or cutting medium is used. The surfaces show no smearing (checked by X-ray crystallography and electron microscopy) and no chemical change in the surface material or in the residue

created. It is unique to B_4C; other gas bearing ceramic materials have seized or spalled when this technique is applied. This micro-machining technique yields a surface finish incapable of measurement by standard techniques. but light reflection indicates the degree of fineness, and both transmission and scanning electron microscopy show surface details and lack of irregularities.

Further studies are underway to determine the mechanical and/or chemical actions taking place on a microscopic scale.

SECTION G

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 in the Solid State Division of the Laboratory.

Sponsorship

The Lincoln Laboratory is a center for research operated by Massachusetts Institute of Technology with 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, MIT (1969: 1, 2, 3 and 4) and in individual publications.

A. L. McWhorter, "Light Scattering from Plasmons in Semiconductors, Proceedings International Advanced Summer Physics Institute (Plenum, N. Y., 1969).

A. L. McWhorter and P. N. Argyres, "Raman Scattering from Magnetoplasma Waves in Semiconductors," Proceedings IX International Conference on Physics of Semiconductors, Moscow, 1968 (Nauka, Leningrad, 1969), Vol. 2.

A. L. McWhorter and P. N. Argyres, "Raman Scattering from Magnetoplasma Waves in Semiconductors," Proceedings of the International Conference on Light Scattering Spectra of Solids, (Springer-Verlag, N. Y., 1969).

A. L. McWhorter, "Light Scattering from Plasmons in Semiconductors," Electronic Structures in Solids (Plenum, N. Y., 1969).

Theses:

N. D. Strahm, "Raman Scattering in Mixed Semiconductors," Ph. D. Thesis, Department of Electrical Engineering, MIT, February 1969.

E. J. Tichovolsky, "Oscillatory Magnetoreflection from Bismuth-antimony Alloys," M. S. Thesis, Physics Department, MIT, February 1969.

RESEARCH REPORTS

1.0 Solid State Theory

Dr. H. J. Zeiger, Leader
Dr. M. M. Litvak, Assistant Leader

Staff Members:

Dr. R. A. Bari
Dr. R. W. Davies
Dr. G. F. Dresselhaus
Dr. T. A. Kaplan
Dr. W. H. Kleiner
Dr. D. M. Larsen
Dr. K. L. Ngai
Dr. A. R. Wilson
Dr. C. Y. Young

Graduate Student Research Assistants:

S. R. Chinn, Electrical Engineering

Research Report:

The Fourier expansion method has been applied to a description of the energy bands of Cu. Good agreement was obtained with observed Fermi surface properties, and with the frequency-dependent dielectric constant.

A theoretical calculation of the energy levels of a polaron in a magnetic field in the intermediate and strong coupling limit has been made. The results are in agreement with experimental observations of cyclotron resonance in CdTe, and allow a determination of the polaron coupling constant.

The characteristics of an intense light pulse propagating in self-trapped filaments through liquids with large optical Kerr constant have been studied. The theory predicts a broadened, frequency-modulated spectrum, agreeing well with experimental observations.

Two magnon Raman scattering has been studied in the perovskite crystal $KNiF_3$, and in the two dimensional layered compound K_2NiF_4. The positions and line shapes for the spectra are in excellent agreement with the theory, based on one exchange parameter determined from the antiferromagnetic ordering temperatures.

A treatment of multiphonon Raman scattering with resonant or near-resonant intermediate states has been developed. The theory seems capable of explaining observations made in a number of semiconductor crystals.

The high temperature expansion for the staggered susceptibility of a two dimensional antiferromagnet indicates that a transition should take place to an ordered state at a finite temperature. The crystal K_2NiF_4 represents an almost ideal example of such a case, and shows a transition at a temperature in excellent agreement with that predicted by the high temperature expansion method.

An application of diagrammatic techniques has been made to the calculation of the coefficients of a transport equation for dynamically independent electrons in the presence of dilute random impurities. The coefficients of the transport equation are given for arbitrary wavelength and frequency of the electric field, and strong single center potentials.

Interstellar grains, which are responsible for the extinction and polarization of starlight, might be important sources of millimeter wave emission from condensed galactic clouds if the grain material resembles a semiconductor with conductivities in the range of .01 to 10 $(\text{ohm-cm})^{-1}$. About 10^{-24} watts m^{-2} Hz^{-1} at the top of our atmosphere would come from opaque, arc-minute regions with column-densities of about 10^{12} grains cm^{-2}, while cooling of the grains by such emission results in temperatures as low as 10°K.

Publications:

S. R. Chinn, H. J. Zeiger and J. R. O'Connor, "Raman Scattering by Magnetic Excitations in $RbNiF_3$," J. Appl. Phys. 40, 1603 (1969).

G. Dresselhaus and M. S. Dresselhaus, "Interpolation Methods for Phonon Spectra in Crystals," Int. J. Quan. Chem. IIS, 333 (1968).

G. Dresselhaus, "Fermi Surface and Optical Properties of Copper," Solid State Commun. 7, 419 (1969).

G. Dresselhaus and M. S. Dresselhaus, "Fourier Expansion for the Deformation Potential in the Diamond Lattice," Proceedings of the IX International Conference on the Physics of Semiconductors, Moscow, 1968 (Nauka, Leningrad, 1969).

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J. Hanus, "Influence of the Molecular Interaction on the AC Kerr Effect: Possibility of a Field-Induced Phase Transition," J. Quan. Elec. QE-4, 753 (1968).

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W. H. Kleiner and T. A. Kaplan, "Symmetry of the Ground Level of a Hamiltonian," J. Math. Phys. 10, 236 (1969).

W. H. Kleiner, "Space-Time Symmetry Restrictions on Transport Coefficients. III. Thermogalvanomagnetic Coefficients," Phys. Rev. 182, 705 (1969).

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D. M. Larsen, 'Effective Mass Theory for Polarons in External Fields," Phys. Rev. 180, 919 (1969).

M. M. Litvak, B. Zuckerman and D. F. Dickinson, "Conditions for Microwave Radiation from Excited OH Λ-Doublet States," Astrophys. J: 156, 875 (1969).

M. M. Litvak, "Infrared Pumping of Interstellar OH," Astrophys. J. 156, 471 (1969).

M. M. Litvak, "Hydroxyl and Water Masers in Protostars," Science 165, 855 (1969).

M. M. Litvak and P. R. Longaker, "Perturbation of the Refractive Index of Absorbing Media by a Pulsed Laser Beam," J. Appl. Phys. 40, 4033 (1969).

M. M. Litvak, "Millimetre Wave Emission by Interstellar Dust," Nature 223, 1143 (1969).

J. L. Sigel and P. N. Argyres, "Transport Equation for Interacting Fermions in Random Scattering Centers. I. A Quasiparticle Description in the Macroscopic and Low Temperature Limit," Phys. Rev. 178, 1016 (1969).

H. E. Stanley, "Spherical Model as the Limit of Infinite Spin Dimensionality," Phys. Rev. 176, 718 (1968).

H. E. Stanley, "Critical Phenomena in Heisenberg Models of Magnetism," Solid State Physics, Nuclear Physics and Particle Physics (W. A. Benjamin, Inc., 1968) Chap. 14, p. 831. Proceedings Ninth Latin American School of Physics.

H. E. Stanley, "Exact Solution for a Linear Chain of Isotropically-Interacting Classical Spins of Arbitrary Dimensionality," Phys. Rev. 179, 570 (1969).

H. E. Stanley, "Some Critical Properties of Quantum-Mechanical Heisenberg Ferro- and Antiferromagnets," J. Appl. Phys. 40, 1546 (1969).

R. A. Bari and R. V. Lange, "The Hubbard Model: Insulator or Conductor for Narrow Band Regime?", Physics Letters A (in press).

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J. L. Sigel and P. N. Argyres, "Transport Equation for a Fermi System in Random-Scattering Centers. II. Independent Electrons in an Arbitrarily Varying Electric Field and Strong Single-Center Potentials," Phys. Rev. (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.
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. J. W. Pierce
Dr. P. M. Raccah
Dr. T. B. Reed
Dr. F. T. J. Smith
Dr. J. M. Steininger

Graduate Student Research Assistants:

R. J. Temkin, Physics

Research Report:

Several techniques have been used to investigate the phase diagrams of binary and ternary systems involving semiconducting compounds and their alloys. The liquidus and solidus curves of the CdTe-ZnTe and CdTe-CdSe systems have been determined by thermal analysis. A simple expression has been derived for the relationship between liquidus and solidus compositions for these and similar alloy systems. X-ray diffraction analysis has shown that in the CdTe-CdSe and ZnSe-CdSe systems the phase diagram below the solidus consists of regions of hexagonal and cubic structure, separated by a narrow two-phase region whose boundaries are markedly temperature dependent. This technique has also provided evidence that in the Bi-Te system at 450°C there is a continuous sequence of closely related

phases, without intervening two-phase regions, between 50.0 and 57.0 at .% Te. Optical absorption measurements on the vapor phase have been used to determine, as functions of composition and temperature, the Zn and Te_2 partial pressures over ZnTe and the Te_2 partial pressures over Bi_2Te_3 and other condensed phases in the Bi-Te system.

Hall coefficient and resistivity measurements have been made on four II-VI compounds at temperatures up to 1000°C under controlled partial pressures of the constituent elements. The dependence of carrier concentration on partial pressure near the metal-rich limit of the homogeneity range gives evidence for the following native defects: a doubly-ionized acceptor in ZnTe, a singly-ionized donor in ZnSe, and doubly-ionized donors in CdTe and CdSe. For each of these compounds, the compositions along the metal-rich solidus over the temperature range studied have been found by extrapolating the carrier concentration vs. pressure isotherms. Data near the Te-rich stability limit give evidence for neutral native defects in ZnTe (probably Te interstitials) and indicate that foreign impurities rather than native acceptor defects are responsible for the formation of p-type CdTe.

The dependence of energy gap on alloy composition has been determined by means of optical transmission measurements on $ZnTe_{1-x}Se_x$ crystals at 77° and 300°K and on $CdTe_{1-x}Se_x$ crystals at 300°K. In each case, there is a minimum in the energy gap at $x \sim 0.4$. In the $CdTe_{1-x}Se_x$ system, for a given composition the energy gap is about 0.03 eV larger for the hexagonal structure than for the cubic structure.

Single crystals of the magnetic semiconductors EuO, EuS, EuSe, and EuTe (with melting points above 2200°C) have been grown by directional freezing of stoichiometric melts and metal-rich solutions in sealed tungsten crucibles. Transparent, resistance-heated furnaces have been constructed for vapor crystal growth at temperatures up to about 1100°C. Conventional insulation is replaced by a layer of gold, deposited on Pyrex, which is highly reflecting in the infrared but thin enough to transmit in the visible.

Our discovery of the ability to transform perovskite-related structures under pressure to new, potentially more useful, phases that are metastable at room temperature and atmospheric pressure prompted us to continue studying a number of these phases. ABX_3 compounds with perovskite structure consist of AX_3 layers cubically stacked and having B cations in corner-shared X-octahedra. Hexagonally stacked AX_3 layers form a two-layer (2L) structure with B cations in chains of face-shared octahedra parallel to the c axis. Hydrostatic pressure or variation of the relative atomic sizes transforms the 2L structure to perovskite via three intermediary structures having different ratios of hexagonal to cubic stacking. The stabilities of these intermediate phases arise from a balance between electrostatic and stacking energies. The magnetic properties of several ferrimagnetic 6L

$CsBF_3$ compounds were studied for possible applications at 10.6 μ. Single crystal of the perovskite $KNiF_3$ and 6L $RbNiF_3$ were grown for Raman studies.

Another large class of perovskite related compounds has the formula $A_{1+x}BX_{3+x}$ (x = 0, 1/3, 1/2, 1), and single crystals of tetragonal K_2NiF_4 were also prepared for Raman studies. $SrIrO_3$, which forms a distorted 6L structure at atmospheric pressure, transforms to perovskite at 45 kbars and 1000°C. $Sr_4Ir_3O_{10}$ (x = 1/3) and $Sr_3Ir_2O_7$ (x = 1/2) were prepared under pressure at 1000°C.

VO_x and TiO_x have a rocksalt structure with about 15% vacancies at x = 1.0 and a rather large solid-solution phase field ($0.8 \leq x \leq 1.3$). The vacancies remain disordered in VO_x, but in TiO_x they can order for $x \approx 1.0$. Several magnetic, structural and transport properties of cast ingots were investigated as a function of x as part of a continuing study of narrow-band electrons. TiO_x is a superconductor whereas VO_x is not. VO_x is semiconducting for all $x > 1.0$ and exhibits exchange enhanced paramagnetism, but no magnetic order and no semiconductor ⇄ metallic transition.

The "bronzes" $M_x^+V_2O_5$ form another group of vanadium oxides that are of interest for the study of localized versus itinerant d electrons. From careful x-ray studies done at the University of Bordeaux, it was possible for us to identify molecular V-O-V units within the structure and to show how these modify the statistics required for calculation of the Seebeck coefficients in a small-polaron model.

Absolute x-ray form factors of Ni and Fe were measured to high precision. The charge density of Ni reflects aspherical d orbitals. Preliminary results for Fe indicate similar distortions from the free-atom form factors as a result of the crystalline fields. These measurements are particularly important for testing band calculations, because the form factor is a ground state property of the atom.

Laser technology has created a renewed interest in transparent transition-metal and rare-earth oxides. Several new tellurates and antimonates have been prepared and characterized structurally and optically. One group has the $PbSb_2O_6$ structure: $M^{2+}BTeO_6$ and $R^{3+}BSbO_6$, where R^{3+} is a rare-earth ion and B = Ge, Sn or Ti. Compounds with the ilmenite structure include $M_2^+BTeO_6$ and $LiCdM^{3+}TeO_6$, where $M^+ = Li^+$ or Na^+ and $M^{3+} = Cr^{3+}$ or Ga^{3+}. The compounds Na_2BTeO_6 having B = Mn or Sn crystallized in an hexagonal structure that has not yet been identified. Compounds with the Na_2SiF_6 structure were also found: $MnSb_2O_6$, $MnBTeO_6$, $M_2^{3+}TeO_6$ where B = Ti or Sn, and M^{3+} = In, Sc, or Lu.

Other compounds that have been prepared and investigated structurally and magnetically include the ruthenium spinels Co_2RuO_4, $ZnCoRuO_4$, and α and β forms of anhydrous $VOSO_4$, and the thiospinel $Cu_{0.5}Fe_{0.5}[Cr_2]S_4$.

Several methods of quantitative chemical analysis have been developed or improved. All four elements in $(Pb_{1-x}Sn_x)(Te_{1-y}Se_y)$ alloys have been determined

by means of electron microprobe analysis. An iterative computer procedure is used to process the x-ray intensity data. The precision of determining metallic elements by means of EDTA titrations with color change end points has been increased to 1-3 parts per thousand by using a spectrophotometer for manual and in some cases automatic titrations. The technique for mass spectrographic analysis of frozen aqueous solutions has been improved by using a nickel sample cup and platinum counterelectrode. It should now be possible to determine almost all elements in solution at the level of 10 parts per million (atomic) or higher.

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3.0 Solid State Physics

Dr. J. G. Mavroides, Leader
Dr. G. B. Wright, Assistant Leader

Staff Members:

Dr. J. W. Allen
Dr. F. A. Blum
Dr. R. C. Brandt
Dr. P. P. Crooker
Dr. M. S. Dresselhaus (part time)
K. Dwight, Jr.
Dr. H. R. Fetterman
Dr. S. H. Groves
Dr. V. E. Henrich
Dr. E. J. Johnson
Dr. W. E. Krag
Dr. J. Melngailis
N. Menyuk
Dr. K. W. Nill
Dr. A. S. Pine
Dr. W. J. Scouler
Dr. R. Weber

Graduate Student Research Assistants:

J. Waldman, Physics

Research Report:

The research in the Solid State Physics Group may be divided into three categories: (1) band structure, (2) magnetic interactions, and (3) scattering experiments with lasers.

3.1 Band Structure

The study of interband magnetoreflection from α-Sn has been completed. Possible explanations for the systematic deviation at high photon energies of the theory based on the inverted band structure model have been proposed.

Our previous oscillatory magnetoreflection results on bismuth-antimony alloys in the range of composition $0 < \% \text{ Sb} < 15$ have been complemented by measurements of additional alloys. Measurements indicate the motion of some of the energy bands in the alloys and permit an identification of the L-point energy bands involved in

transitions in pure bismuth with those involved in pure antimony. The results suggest a pattern for the variation of the energy bands at the L- and T-points in the Brillouin zone for the bismuth-antimony-arsenic system which is consistent with all previous magnetoreflection data in these semimetals.

A comprehensive magneto-optical investigation of the conduction band of InSb has been carried out. Aside from the fundamental cyclotron resonance transitions, additional transitions involving impurities, spin-flip, cyclotron resonance harmonics and phonons were investigated.

Studies by optical reflectance of magnetic ordering effects in the magnetic semiconductors EuO, EuS and EuSe, have provided evidence that conduction band is spin-polarized in the ferromagnetic state; the low energy peak E_1 at ~ 1.5 eV is due to $4f^7 \rightarrow 4f^6 5d(t_{2g})$ transitions and the higher peak E_2 at ~ 4 eV is due at least in part to $4f^7 \rightarrow 4f^6 5d(e_g)$ transitions. Similar measurements have also been made on EuTe which is antiferromagnetic below 10°K. In this case the reflectance is strongly field dependent at the lower fields. At high fields (above 60 kOe) the E_1 structure has a form identical to that of ferromagnetic EuO, EuS and EuSe and this is taken as evidence for field induced spin alignment in EuTe.

Zeeman experiments on hydrogen-like centers induced in AgBr by ultraviolet light have revealed a mass shift due to electron phonon interaction which is enhanced by the close proximity of the transition to the longitudinal optic phonon energy. The anomalous energy of the phonon needed to explain the effect is leading to a reinvestigation of polaron theory.

Electron-phonon interactions were also investigated in CdTe with cyclotron resonance measurements at discrete laser and carcinotron wavelengths between 118 and 901 μ. The effective mass of the polarons was found to vary in the manner predicted from a variational calculation of the lowest Landau level energies.

Extension of the low temperature stress measurements on phosphorus-doped silicon to more homogeneous and higher stresses (up to 17.5×10^8 dynes/cm^2), about three times that of earlier experiments, has resulted in a significant improvement in the impurity optical spectra. This has allowed the observation of a nonlinear energy shift of the transition energies which is explained theoretically by the downward shift with stress of the ground state.

Shubnikov-deHaas measurements under hydrostatic pressure (up to 8 kbars) have been carried out in $Pb_{1-x}Sn_xTe$ alloys of composition $0.16 \leq x \leq 0.32$. The shape of the Fermi surface appears not to change with pressure, although there is a decrease of the cyclotron effective masses.

A study has been initiated of electron tunneling through insulating films into PbSe with emphasis on the effects of the optic phonons. The instrumentation has been checked out on GaAs, and preliminary measurements have been obtained in p-type PbSe.

3.2 Magnetic Interactions and Ordering

An investigation of the magnetic interactions in the ferromagnetic conducting alloys $CoS_{2-x}Se_x$ has been initiated. Preliminary measurements in the magnetic transition region for x = 0.1 and 0.2 have raised some questions regarding the order of the phase transition; it is hoped that differential thermal analysis may resolve this point. Concurrent with this experimental work, a theoretical study was carried out of the spin configuration which minimizes the classical Heisenberg exchange energy in the fcc lattice with first- and second-neighbor interactions. The results are in contradiction to the spin configurations of CoSeS and $CoSe_2$ proposed by Adachi, et al., from neutron diffraction. If the latter configurations are correct, then there must be significant contributions to the energy from other than Heisenberg interactions.

Investigation of the local stability of the conical spiral spin configuration in normal cubic spinels shows that the spiral which gives good agreement with experiment for $CoCr_2O_4$ is actually unstable for the estimated values of the nearest-neighbor A-A, A-B, and B-B, and more-distant-neighbor B-B exchange interactions. The results demonstrate the existence of a new, previously unimagined configuration having nonzero Fourier components associated with more than one member of the $\vec{k} = (h, h, 0)$ family -- a configuration which appears to be more complicated than an epicone spiral.

Various aspects of neutron diffraction experiments yield conflicting results as to the order of the ferrimagnetic-antiferromagnetic transition in Cr_5S_6. In order to resolve this apparent contradiction, Cr_5S_6 is being examined theoretically, by means of the Heisenberg Hamiltonian, and experimentally, by investigating its magnetic properties as a function of pressure as well as magnetic field and temperature.

An investigation has been carried out on the magnetic field dependence (2.5 to 23.5 kOe) of the nuclear resonance linewidth of Mn^{55} in the low anisotropy antiferromagnetic compounds $CsMnF_3$ and $RbMnF_3$ at 18° and 4.2 °K. An interpretation of the linewidth behavior in terms of existing theories gives fair agreement except for an unexplained anomalous linewidth peak which is observed only in $RbMnF_3$.

Measurements from 5.0 to 70.0 GHz of the intensities of the spin wave absorption peaks of two nickel-iron films indicate that the spin wave dispersion is quadratic in mode number, p, from p = 9 to 21, with a frequency dependent normalized intensity behavior which approaches $1/p^8$ to $1/p^{11}$ rather than $1/p^2$. Since mode number assignment for these films was unambiguous, the odd-integer numbering scheme (and surface spin pinning) cannot be invalidated, as recently suggested in the literature, simply on the basis of the deviation of the intensities from $1/p^2$ behavior. Furthermore, any intensity model must include the strong frequency dependence.

The spin-space group concept, advanced by Brinkman and Elliott for analyzing

the symmetry properties of spin waves in magnetic insulators where spin-orbit coupling effects are negligible for the ground state of the magnetic ion, can be extended to optical excitons arising from single-ion transitions between the ground state and an excited state where spin-orbit effects are negligible. This idea has been applied to the $^4A_2 \rightarrow {}^2E$ excitons in Cr_2O_3 to investigate the role of spin-orbit coupling in producing the small but nonzero measured transfer-of-excitation matrix elements between opposite spin sublattices.

A new type of electron spin wave in conducting solids resulting from spin orbit coupling, and distinct from Fermi liquid spin waves, has been described. It is expected that these waves will be observable by Raman scattering experiments.

3.3 Scattering Experiments with Lasers

Using Brillouin spectroscopy, the velocity and attenuation of 27 to 28 GHz longitudinal hypersonic waves in fused quartz have been measured between 80° and 600°K. The pronounced attenuation peak at ~ 130°K, also observed previously by ultrasonic measurements but attributed to a structural relaxation mechanism, can be explained by a simple anharmonic mechanism involving scattering of thermal phonons.

The high-resolution thermal Brillouin scattering technique has been used to study the temperature dependence of the hypersonic (3- to 5-GHz) velocity and attenuation in liquid nitrogen along the saturated vapor line from the triple point to the normal boiling point. Since both the velocity and attenuation results agree with previous measurements at megahertz frequencies, the acoustical dispersion due to the 2-GHz internal molecular vibration frequency is completely negligible.

Fine structure, which is a manifestation of an allowed linear dependence of the optical phonon frequency with wavevector, has been observed in the low temperature Raman spectrum of the 128 cm^{-1} E-mode in α-quartz. The optical activity which should be associated with this linear wavevector shift has been calculated. A linear wavevector dispersion was also observed in the transverse acoustic branches via backward Brillouin scattering.

The cross section for the inelastic scattering of light from mobile carriers in semiconductors in a dc magnetic field has been calculated in a manner sufficiently general to include directly particle-particle Coulomb interaction and important band structure effects. The result is a significant improvement over previous calculations, and yields important screening effects for Landau level Raman scattering.

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4.0 Applied Physics

Dr. J. O. Dimmock, Leader
T. C. Harman, Assistant Leader
Dr. I. Melngailis, Assistant Leader

A. R. Calawa
T. F. Clough
Dr. J. P. Donnelly
Dr. A. G. Foyt
Dr. C. E. Hurwitz
Dr. W. T. Lindley
Dr. A. Mooradian
Dr. J. A. Rossi
Dr. D. L. Spears
Dr. G. E. Stillman
Dr. C. M. Wolfe
P. Youtz

Graduate Student Research Assistants:

S. Brueck, Electrical Engineering

R. A. Murphy, Electrical Engineering
M. R. Oliver, Electrical Engineering

Research Report:

Guard-ringed GaAs Schottky barrier diodes have been fabricated which exhibit uniform avalanche photocurrent gains exceeding 100 with gain-bandwidth products over 50 GHz. The diodes consist of semitransparent platinum Schottky barrier contacts electroplated on n-type GaAs. The insulating guard ring was formed by proton radiation bombardment. Operating at a gain of 100 the photoresponse was uniform across the active region of the diode to better than ± 20 percent, and the response speed was less than 0.3 nsec.

Efficient doping of GaAs has been observed using Se^+ ions implanted at 400 keV, and high quality n-p junctions have been obtained using this technique. For a Se^+ dose of $3x10^{12}/cm^2$ giving a peak carrier concentration of $2x10^{17}/cm^3$, more than 50% of the implanted ions were observed to be electrically active. For larger doses the doping efficiency decreases, and the carrier concentration approaches a limiting value of approximately $10^{19}/cm^3$. GaAs n-p avalanche photodiodes fabricated in this manner have shown photocurrent gains in excess of 300 when biased near reverse breakdown. As in the Schottky barrier devices, a guard ring of insulating GaAs was formed by proton bombardment. Again the photoresponse was found to be uniform over the entire region of the diode to better than ± 20 percent at an average photocurrent gain of 100.

Spectral measurements have been made on electroluminescent metal-insulator-semiconductor diodes fabricated from p-type ZnTe. The insulating region was created in the ZnTe by proton bombardment and gold was used for the metal contact. Efficient green electroluminescence, associated with the bandgap, and red electroluminescence, associated with an isoelectronic trap, were observed in devices made from different crystals.

Proton bombardment has been found to produce n-type layers in p-type InSb and has been used to fabricate high quality n-p junction photodiodes with resistances at zero bias in the range of several hundred thousand ohms. A peak detectivity of $7.7x10^{10}$cm $Hz^{1/2}/W$ has been observed at 5.3 μ, and an array of 12 diodes has been fabricated on a single wafer, all of which have 500°K black body detectivities in excess of $1x10^{10}$cm $Hz^{1/2}/W$.

The effects of light on the charge state of anodized InSb MOS devices have been further classified. Infrared radiation above 0.23 eV creates electron-hole pairs in the InSb, and starting at about 1.2 eV some of the photoexcited electrons escape and become trapped in the oxide. At photon energies above 3 eV the oxide becomes photoconductive, such that its charge state can be modified by applying bias, and the

surface of the n-type InSb can be swung from accumulation to inversion in a controlled fashion.

Epitaxial layers of GaAs with 77°K Hall mobilities up to 210,000 $cm^2/Vsec$ have been grown in an $AsCl_3$-Ga-hydrogen flow system. The best sample had a peak mobility of 340,000 $cm^2/Vsec$ at 40°K and a total ionized impurity concentration of about $7x10^{13}cm^{-3}$. The total ionized impurity densities were obtained from analyses of the temperature variation of the Hall constant, and also by analyzing mobility and carrier concentration data as a function of temperature using the Brooks-Herring formula. These results have been used to determine empirical curves relating the impurity density to the 77°K Hall mobility and carrier concentration measured at 5 kG.

The temperature and magnetic field dependence of the Hall coefficient factor for polar optical mode scattering has also been measured in the high purity n-type epitaxial layers of GaAs. The experimental variation is in fair agreement with theoretical calculations.

Spectral measurements of the far infrared photoconductivity due to shallow donors in GaAs reveal peaks due to the ($1s \rightarrow 2p$) and ($1s \rightarrow 3p$) transitions in addition to a broad continuum at higher energy. From the energy of these transitions and their splitting in a magnetic field we obtain a donor ionization energy of 5.86 meV and an effective electron mass of 0.0665 m_o.

The effect of donor concentration on the extrinsic photoconductivity spectra of shallow donors in GaAs has been studied for donor concentrations between $4.8x10^{13}$ and $2x10^{15}cm^{-3}$. The ($1s \rightarrow 2p$) photoconductivity peak remains essentially constant while the measured thermal ionization energy decreases with increasing donor concentration due to the merging of the higher excited impurity states with the conduction band edge.

Far infrared radiation corresponding to transitions from excited donor states and from conduction band states to the ground state of a shallow donor has been observed in high purity epitaxial layers of GaAs at 4.2°K. The emission has a main peak at 282 μ and a broad continuum extending to higher photon energies. A total radiated power of 10^{-7} watts has been observed.

The temperature dependence of the energy of laser emission from $Pb_{1-x}Sn_xSe$ diodes in the composition range $0 \leq x \leq 0.3$ has been studied up to 100°K. For $0 \leq x \leq 0.15$ the dependence is positive above 30°K, whereas for $0.15 < x \leq 0.3$ the dependence is negative. This is consistent with the band model proposed in which the conduction and valence bands invert at about $x = 0.15$.

In addition, the magnetic field dependence of the energy of laser emission from $Pb_{1-x}Sn_xSe$ diodes in this composition range has been studied at 4.2°K. For $0 \leq x < 0.15$ the magnetic field dependence is positive for the lowest energy line, whereas for $0.15 < x \leq 0.3$ the dependence has about the same absolute value but is negative. This is again consistent with the proposed band inversion model.

Interdiffusion in PbSe has been studied by diffusing excess Se into Pb-rich n-type PbSe and excess Pb into Se-rich p-type PbSe. The results are in essential agreement with a diffusion model in which the interdiffusion coefficient has two values, D_p in Se-rich material and D_n in Pb-rich material with $D_p = 9D_n$.

The conductivity of the ferromagnetic semiconductor EuO has been measured as a function of temperature and magnetic fields. The resistivity exhibits a sharp increase between 50 and 70°K, which is interpreted in terms of a transfer of electrons between a conduction band whose energy position is a strong function of temperature and magnetic field and a trap whose energy is roughly constant.

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CENTRAL FACILITIES OF THE INTERDISCIPLINARY LABORATORY

The Central Facilities in the Interdisciplinary Laboratory provide two types of service to the research groups associated with the Center. General services for chemical analysis, machine shop work, electronic instrument repair, computation facilities, reading room and technical information on materials are established under professional supervision. Specialized services for crystal growth, materials preparation, and materials characterization are established under the direction of a faculty member who is actively engaged in research in the same field. The capabilities of these specialized services made available to members of the Center and others at MIT are maintained at the forefront of the art by this close association with the research programs conducted by the supervising faculty member.

The Central Facilities are described briefly below:

GENERAL SERVICE FACILITIES

Central Analytical Laboratory

Staff:

A. F. Witt, Associate Professor
L. A. Carrara, D.S.R. Staff
D. L. Guernsey, D.S.R. Staff
S. M. Nagy, D.S.R. Staff
W. W. Correia, D.S.R. Staff
E. Neuwelt, Technical Assistant
C. A. Clark, Northeastern University Cooperative Student
S. Benson, Northeastern University Cooperative Student

The Central Analytical Laboratory provides chemical - analytical service throughout the Institute and is engaged in improving existing and in developing new analytical techniques in order to meet the continuously changing requirements put forward by materials research. In line with these developments the Analytical Laboratory shifted emphasis from predominantly "wet" chemical analysis to instrumental semi-micro and microanalysis.

During the past year over 2500 analyses were performed by the laboratory for some 150 projects. These analyses were predominantly for the M.I.T. community, including the Instrumentation Laboratory, the Lincoln Laboratory, and the National Magnet Laboratory. The facility was, however, also used by other institutions including Harvard University, University of Pennsylvania, and the University of Connecticut.

The scope of analytical work ranged from routine metallurgical specimens (bulk and trace analysis) to laser and semi-conductor materials in which trace impurities had to be qualitatively and quantitatively analyzed. In some instances the analytical laboratory served also as consultant and assistant to various groups requiring analytical services.

The Analytical Laboratory is also extensively engaged in analyses of liquids and gases in particular of various gases dissolved in trace amounts in metals and alloys.

A partial list of the instrumentation available at the Central Analytical Laboratory includes the following:

Emission spectrograph
Atomic absorption spectrograph
Beckman Spectrophotometer with flame photometer attachment
Photofluorometer
Controlled potential Electro-analyzer
Orion Ion analyzer
Sargent polarograph
Gas Chromatograph
Leco gas analyzers for H_2, O_2, N_2, and C

Since the Laboratory is supported by the Center for Materials Science and Engineering it is possible to keep the charges low and as a result they compare favorably with those of commercial analytical facilities. In many instances these charges are based on the amount of time spent on the project. The more common metallurgical analysis are performed at standard charges. Specific information concerning these is available upon request.

Central Machine Shop

Staff:

P. Kelleher, Foreman
T. Farrell
W. Fielding
E. Gempka
C. Desjardin
E. Newman
F. Payne
G. Shawnessy

The facility is a fully equipped shop staffed by 7 machinists established to construct, modify or repair the wide variety of apparatus used in the center. Much time is devoted to student thesis work and a high priority has been given to work of this nature. In the 1968-69 period 75 projects have used our facilities with over 400 requisitions for services. The machinists are highly skilled and can often contribute solutions to design problems.

Machine Tools available include:
High Precision Lathes (Max. turning capacity 16 1/2") for turning, boring thread cutting including metric pitchs.
Milling Machines equipped with dividing heads and rotary tables for angular indexing of holes, grooves, graduations etc.
Surface Grinders maximum capacity 6" x 18"
Cylindrical Grinding maximum capacity 5" x 15"
Internal Honing 1/8" - 2" dia.
Drills 0" - 1" larger holes may be cut in plate
Band Saw 24" capacity
Sheet Metal Tools include a 48" shear 24" box brake 2" x 24" slip roll

Miscellaneous services include heat treatment, welding and hard and soft soldering. A student-staff shop located in rm. 13-2045 is maintained as part of this facility.

Electronic Instrument Repair and Construction Shop

E. L. Greenwood, Technician

The services performed by this shop are the construction of electronic equipment, repair of electronic instruments, and trouble diagnosis. Consultation is offered on electronic problems to staff members, students and other Technicians.

The Electronics Shop (Room 13-1029) is equipped with bench instruments and is available to others for short-term projects. Electronic parts may be requisitioned from the Laboratory Supplies Stockroom (Room 4-052) and the Physics Department Stockroom (Room 4-335)

Central Computation Facility

Staff:

Professor Roy Kaplow, Faculty Supervisor
Miss Sally Duren, Staff Programmer

The Computation Facility of the Materials Center provides computer-related services. Included among these are:

a. Convenient access to general purpose equipment, such as a type 029 keypunch (for punching cards), a remote typewriter terminal (for general purpose access to any of the M. I. T. time-sharing systems), a remote ARDS-II storage-tube terminal (for on-line, graphical input and output).
b. Consultation regarding the use of that equipment and the broader M. I. T. central facilities (IBM 360/65-40, IBM 7094/CTSS, IBM 360/67-CP/CMS, GE 645/MULTICS) and their associated peripheral equipment. Advice may be obtained, also, on problems of program writing.
c. Complete program writing and implementation on a "custom-job" basis.

In addition, the facility attempts to provide a focus for computer-service-oriented development work. It is presently assisting in the implementation of a Literature Search Service experiment (sponsored by the National Science Foundation) in which about twenty members of the Materials Center Staff are participating, in cooperation with the Technical

Information Project.

Materials Center Reading Room

Staff:

Mary E. Pensyl, Librarian
Betty-Ann Curtis, Assistant Librarian

The Materials Center Reading Room, which maintains a collection of material supporting the research activities in Building 13, has been in service since November 22, 1965. It is operated administratively as a branch of the Engineering Library with partial support from the Advanced Research Projects Agency. The Reading Room contains a very selective working collection oriented toward solid state physics and material science, having current research value to staff members in the Center. A Library Committee representing the various Center disciplines meets periodically with the Librarian to choose material recommended by members of the Center. The present Committee, chaired by Professor G. B. Benedek (Physics), includes: Professor R. B. Adler (Electrical Engineering); Professor M. B. Bever (Metallurgy); Professor G. F. Koster (Physics); Professor F. R. Morgenthaler (Electrical Engineering) and Professor D. P. Shoemaker (Chemistry).

Immediate availability of items in the Reading Room is of prime concern; therefore, it is a reserve collection, circulating only during hours that the Reading Room is closed. However, all purchases made for the Reading Room are duplicated in the Engineering Library, where material can be borrowed for the standard loan period. Seating capacity in the Reading Room remains at 14.

There are 1,100 monograph and serial titles and 91 periodical titles. A yearly statistical compilation of reader use determines the renewal policy for journal subscriptions. Limited holding of standard abstracts and indexes are available for literature searching. An archive collection of 630 reports and publications written by members of the M.I.T. community and supported by the Center for Materials Science and Engineering is housed in a file cabinet and indexed in the card catalog. Annual reports from 24 major materials research centers throughout the United States are also available.

An Addressograph-Multigraph 300 Electrostatic Copier is located in the Reading Room for copying library material, supplemented by a Xerox facility across the corridor. Copies can be charged to an Institute operating

account.

The services of the Reading Room include: Literature searching; compiling of bibliographies and maintaining current awareness for staff members. A bulletin is periodically published giving an annotated listing of recent acquisitions, library news and information on materials science literature. Three hundred copies of each issue are regularly distributed throughout the Center as well as to interested parties outside the Institute. Furthermore, the Reading Room serves as a liaison between Materials Center personnel and the Defense Documentation Center, specialized data analysis centers and other referral services. Heavy use of this facility attests both to its convenience and its relevance to the needs of the members of the Center for Materials Science and Engineering.

Technical Information Services

E. P. Warekois, Research Staff

A Technical Information Services has been established to act as a liaison between the various material oriented groups within the Center for Materials Science and Engineering, the M.I.T. Lincoln Laboratory, and the Francis Bitter National Magnet Laboratory. The primary function of this service is to collect and provide information relative to the availability or sources of requested research materials, unique processing facilities, or specialized measurement techniques that exist throughout the M.I.T. materials community. It is hoped that this type of service will encourage more interaction between those individuals involved in producing such materials and those individuals involved in the characterization of materials.

SPECIALIZED SERVICE FACILITIES

Insulating and Optical Crystal Growth Facility

Staff:

A. Smakula, Professor, Electrical Engineering
A. Linz, Research Associate, Electrical Engineering
J. Kalnajs, Research Physical Chemist, DSR Staff
V. Belruss, DSR Staff
E. F. Farrell, DSR Staff
D. R. Gabbe, DSR Staff (part-time)
R. Mills, Project Technician
A. Vetrovs, Technical Assistant

This facility is equipped to handle the chemical synthesis, crystal growth, sample preparation and characterization of most types of oxides, fluorides and other halides, utilizing many different techniques. This is made possible by having a sizeable staff with diverse skills, each devoting a part of his time to the facility and the rest to the Crystal Physics and Optical Electronics Laboratory.

During the past few years the Insulating and Optical Crystal Growth Facility has provided crystals for many groups within the Materials Center and the rest of MIT, as well as providing a great deal of consulting effort on crystal growth and crystal characterization. Crystals have also been provided to laboratories outside MIT, including other universities, Bell Telephone Laboratories, Brookhaven National Laboratories, and others. We welcome opportunities to expand our field of operations and enter into cooperative research with other groups within the Institute.

1. Chemical Synthesis

Chemical preparation

Calcination

Purification

Zone refining

Dry box

Chemical preparation of feed materials of halides, fluorides 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 halides. A more elaborate zone refiner for the purification of more refractory materials is under development. There is also a dry box for handling

deliquescent halides and fluorides and equipment for pulverizing and classifying flame fusion oxide feeds.

2. Crystal Growth

The crystal growth facilities include baths for growth from aqueous solution, which are loaned out to laboratories who wish to use them. A Tem-Pres two reactor system capable of operating at temperatures up to 800°C and pressures of 10,000 psi is available for hydrothermal growth from aqueous solution. Halide crystal growth is accomplished with either a low temperature Bridgman furnace using sealed quartz crucibles, or a Czochralski furnace with atmosphere control. Fluoride crystals can be grown in atmosphere controlled Czochralski furnaces permitting crystals of extremely high quality to be obtained. The growth of refractory oxide crystals by melt techniques is accomplished by the use of either a flame fusion burner or an RF powered high temperature Czochralski furnace. Oxide crystals may also be grown from fluxes using one of three furnaces for slow cooling of sealed crucibles. Where suitable, a top-seeded solution growth technique developed at this laboratory is available for the production of very high quality oxide crystals, particularly ferroelectrics and laser host materials. There are currently 5 furnaces available for this type of growth. A chemical vapor deposition (CVD) furnace has recently been added to the facility for growth from the vapor, and it is expected that other more complex vapor phase crystal growth systems will be added.

Solution growth

Hydrothermal

Halides

Fluorides

Oxides

Flux growth

TSSG oxides

Chemical vapor deposition

3. Crystal Characterization

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.

Density

X-ray diffraction	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 Cary-14R high-resolution spectrophotometer in the ultraviolet, visible, and near infrared. There is also a Beckman IR-12 available for infrared measurements, making possible measurements over the range from 1860 Å to 50 microns. Equipment for precise measurement of refractive indices of crystals over a wide wavelength range is being added to the facility. Steady state optical fluorescence spectra, excitation spectra and lifetime measurements can be made over the range from 3,000 Å to 2.5 microns at temperatures between $4^{o}K$ and $500^{o}K$. For the preparation of specimens, x-ray and optical orientation as well as cutting, grinding and polishing of crystals can be carried out. There is also a vacuum evaporator available for electroding specimens for electrical measurements and other purposes.
Spectrophotometers ultraviolet visible infrared	
1860 Å → 50 μ	
Refractive index	
Optical and infrared fluorescence	
X-ray orientation	
Cutting, grinding and polishing	
HV evaporator	

4. Charging Policy

Extensive use of the Crystal Physics Laboratory facilities by students from other laboratories has been encouraged and is a large factor in this operation. Where such students are available to participate in the work we have avoided making any charges for the use of facilities by these students. Where a large crystal growth project involving long-term involvement of the Crystal Physics Laboratory staff is involved, special arrangements are made with the group involved. In some cases, as typified recently by the successful project for the growth of vapor phase crystals of SnO_2 for Professor Rediker's group, the addition of these facilities for vapor phase growth was of sufficient importance that the Capital Equipment was provided from the Central Facility funding, while the labor was provided by a graduate student in Professor Rediker's group. Such mutually beneficial projects are encouraged. All consulting and, where possible, crystal samples that exist on the shelf or which can be grown with known techniques without major development effort, are provided out of Central Facility funding. Only where a major development

effort is required and no student help is available are time and materials charges applied. Up to now, Central Facility funding has proved adequate to cover the cost of maintaining equipment and no charges have been made for use of equipment.

Semiconductor Crystal Growth and Characterization

Professor H. C. Gatos, Faculty Supervisor
Professor A. F. Witt, Faculty Supervisor
M. Lichtensteiger, DSR Research Staff

The Central Facility within the Electronic Materials Group is engaged in the growth of elemental and compound semiconductor crystals in bulk and film form and in extensive work to characterize the electrical and optical properties of these materials.

The purpose of the Facility continues to be twofold: it endeavours to keep abreast of and develops new techniques in materials preparation and characterization within the framework of the "state of the art" and it provides services to meet specific needs for semiconductor crystals on a developmental basis. The characterization of materials properties related to structural perfection, stoichiometry, impurity content and homogeneity is an important part of the activities. Members of the Facility and the Electronic Materials Group are extensively consulting on crystal growth techniques, sample preparation and evaluation.

During the past year the Semiconductor Growth Facility has prepared and supplied various materials in close cooperation with interested groups throughout the Institute, e.g. germanium single crystals with extremely low carrier concentrations for dielectric studies, gallium and indium antimonide crystals for an exploratory investigation of IR window materials, high resolution low temperature sensors employing germanium thin films, and others. Considerable effort has been placed in the preparation and growth of lead salts, urged by the needs of several groups in the Center. A major study of the deposition of thin films by sputtering techniques has led to a clearer understanding of the mechanisms involved and has resulted in a method for type conversion in cadmium sulfide, previously only possible by ion-implantation techniques.

A number of Czochralski furnaces are operating with provisions for growing crystals under vacuum or protective atmospheres including a RF heated puller which permits growth of materials with melting points up to 1500°C. The Facility is supplemented with a horizontal zone melting furnace

a high temperature Bridgman furnace used for the growth of lead salts, an arc melting furnace and a vacuum annealing unit reaching temperatures in excess of 1800°C. The Facility also has at its disposal a RF sputtering system - developed in the group - which is presently employed in a study of structural and electrical properties of cadmium sulfide crystalline films. A modular RF-DC sputtering system has been designed and built which permits rapid change of target materials with minimum contamination of the chamber. A small vacuum coater is available for the deposition of thin films by direct evaporation in the 10^{-6} Torr range, while a high vacuum system capable of reaching limiting pressures of 10^{-9} Torr is currently being tooled for vacuum deposition work. An ultra-high vacuum system which reaches 10^{-11} Torr is also available for the study of properties of "clean" surfaces.

A comprehensive electrical measurement facility has been created for the characterization of electronic materials. It is centered about a 9-inch field regulated magnet with 15 KGauss field intensity. Peripheral equipment has been instrumented to make possible semi-automatic precision Hall and resistivity measurements from liquid helium to room temperatures. Samples up to 400 KOhm impendance can be measured with 0.3 μV resolution. A Van der Pauw set-up with a vibrating capacitor electrometer as detector permits electrical transport measurements on insulating materials and thin films up to at least 10^{10} Ohm samples impedance. Two sets of standardized quick-connect sample holders have been designed around readily available electronic components which greatly enhance the usefulness of the test facility. More recently, the range of transport measurements has been expanded to 900°C with the addition of a high temperature bi-filar wound vacuum furnace.

Equipment for optical reflection and transmission measurements on bulk or film samples using a single beam spectrometer with an optical modulation technique is being assembled. It will resolve weak optical structures by a differential technique in the energy range 6.2 eV to 0.5 eV. Additional optical facilities include a Reichert light microscope and a Zeiss Ultraphot II providing linear magnifications from 4x to 1200x with a resolution exceeding 2000 Å. A transmission interference contrast attachment and a flatness interference tester covering a 3" diameter field of view aid further in the elucidation of optical properties of materials.

The various parts of the Central Facility briefly described have been made available to an increasing number of groups in the Center and other parts of the MIT Community. Due to the specialized nature of the equipment, assignments are either handled by staff and other members of the

group, or appropriate training may first be given with further assistance rendered when needed. Often no charges are made, since the Facility is largely sponsored by the Center for Materials Science and Engineering, however, in some instances nominal charges for materials and labor are being made.

Semiconducting Crystal Preparation Facility

Professor R. H. Rediker, Faculty Supervisor

This facility is equipped to cut and/or polish the large spectrum of semiconductor materials with a minimum of work damage. A Felker O. D. cutting machine with carborundum or diamond impregnated cutoff wheels of up to 8 inches in deameter and with an adjustable orientation table for sample mounting is used to slice boules of relatively hard semi-conductors. A smaller cutting machine with 4-inch diameter diamond impregnated wheel is used to cut smaller boules and also to dice wafers. Two wire saws of unique design are used to cut boules and dice wafers of softer semi-conductors such as the lead salts. The speed of travel of the nichrome wire which carries the abrasive to the sample is fully adjustable as is the down feed onto the sample. True cuts can be made at a cutting rate as slow as one centimeter per day. Oriented cuts are possible with the string saws as they are with the Felker cutting machine and requests for such oriented cuts are honored by use by our facility of the X-ray equipment available in the Metal Crystal Preparation Facility or in the Insulating and Optical Crystal Growth Facility. For cutting odd or cylindrical-shaped samples, a Sheffield 200 watt Ultrasonic Cutter is available. The largest size cutter recommended for this "cookie cutter" is 1 inch in diameter x 3/8 inch deep.

For polishing, four Buehler polishing wheels are used, two of which are inside a chemical exhaust hood so they can be used for simultaneous etching and polish to further reduce work damage. A Struers DP-10 polishing wheel is used for polishing with diamond paste. A metallograph is available to evaluate the results of the polishing.

Preparation of the semiconductor samples is done by a skilled technician upon submission of written requests. The users of the facility are charged an amount tied to the technician's salary for the actual time he works on their project. The present charge is approximately $3.75 per hour. Any charges incurred in sample preparation from other central facilities such as for X-ray orientation are passed on the user. In exceptional cases, where a student or staff member needs to prepare many samples

using one of the less critical pieces of equipment, he will at the request of his professor be taught by the technician in charge to use the equipment and then be allowed to use it when it is not otherwise in use. During the past year the use of this facility can be approximately broken down to 80 percent by Electrical Engineering members of the center, 17 percent by Metallurgy and Materials Science members of the center and 3 percent by members of the M. I. T. community outside the center.

Metal Crystal Growth Facility

Professor M. C. Flemings, Faculty Supervisor

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. Small to medium size quantities of high purity alloys in polycrystalline form can also 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. An induction vacuum melting and pouring furnace and an air melting and pouring furnace are also available.

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, and a plasma beam float-zone crystal grower is used for metal-refractory composite crystals and refractory compounds including refractory metal oxides.

During the past year, a wide variety of specimens and crystals have been prepared for staff members and graduate students. In many cases, graduate students utilized the equipment themselves, with instruction and supervision of Mr. Berry.

Metal Crystal Preparation Facility

Professor B. L. Averbach, Faculty Supervisor
George Pishenin, Engineering Assistant

This facility is equipped to orient, cut and anneal metallic single crystals. The crystals are mounted on goniometers which can be transferred directly to the cutting apparatus, and orientations are obtained by means of X-ray back reflection Laue patterns. Cutting can be accomplished on an abrasive cut-off wheel, a spark cutter, an abrasive string saw and an acid string saw. Simple shapes may also be produced on the spark cutter. An X-ray spectrometer is available for precise orientations of crystal faces. Facilities for annealing to remove the local damage introduced by cutting are also available.

Charges to the user are based on the time consumed on each job.

Ceramic Materials Processing Facility

Professor W. D. Kingery; Faculty Supervisor

The Ceramics Processing Laboratory, located in Room 4-010, has facilities for forming and shaping hard brittle polycrystalline and single crystal materials into complex and precise shapes. Services are available to any department of the Institute on a cost-reimbursement basis. Some materials can be supplied on a no-charge basis, and other materials can be supplied or ordered at cost; however, because of the special requirements of individual users, users of the facility are urged to provide their own materials. Work is accepted as finish drawings or in rough sketch form accompanied by an Institute requisition. Normally two weeks is required for delivery; panic service can usually be provided, sometimes requiring overtime charges.

A partial list of typical jobs is:

1. drilling holes with diameters between .010 and 2.00 inch
2. slotting, coring, dicing, cubing, etc.
3. cylindrical grinding, inside and outside diameters, thread grinding, helical grooving, etc.
4. grinding plane parallel surfaces
5. lapping optical finishes on high-fired, dense ceramics and hard single crystals

6. complex shape sample preparation such as Hall effect samples, masks for vapor deposition, etc.

A partial list of typical materials shaped is:

1. Polycrystalline ceramics such as alumina, zirconia, magnesia, mullite, spinel, pyroceram, porcelain, fused silica, barium titanate, silicon carbide, boron carbide, titanium diboride.

2. Single crystals such as sapphire, ruby, garnet, quartz, zinc oxide, zinc telluride, zinc antimonide, cadmium sulfide, gallium antimonide, lithium fluoride, indium antimonide.

3. Hard metals such as tungsten, tungsten alloys, molybdenum, various intermetallics.

4. Mineral samples such as quartz crystals, feldspar, granite, rock samples, meteorites, coral.

Some machines are available for student use under supervision. These are:

1. air-abrasive unit - cuts small holes and slots, abrades, deburrs and cleans metals, plastics, ceramics, refractory metals, etc.

2. air-rotor drill (industrial dental drill)

3. diamond cut-off saws - make straight cuts on full range of ceramics from talc to sapphire.

The remaining machines, a 10-inch lathe, a milling machine, two drill presses, two surface grinders, two ultrasonic impact grinders, a large band saw, and an automatic lapping machine, all diamond-tool equipped, are restricted to use by trained operators.

Central Facility for Electron Microscopy

Professor J. F. Breedis, Faculty Supervisor
Robert Goss, Project Technician

Studies of materials using high-resolution electron microscopy

methods can be performed in this facility. Equipment includes three electron microscopes (a Siemens Elmiskop I, a JEM-7 and a Philips EM 100B), a high resolution electron diffraction attachment capable of heating to 1000°C, evaporators for the preparation of replicas, devices for different methods of foil preparation, and complete photographic facilities including an automatic-dodging LogEtronics printer. Routine investigations of limited duration can be performed by the technician assigned to the facility. Otherwise, instruction in the use of equipment is provided for those who plan more protracted research programs. All personnel of the facility are available for advice concerning experimental difficulties and intrepretation of results. The expenses of servicing equipment, the wages of the technician and expendable items such as photographic materials, are borne by the users of the facility. The present rate of charge is: $15 per hour for electron microscopy, $10 per hour for the services of the technician in other work such as replica preparation, and $5 per hour for use of facility equipment.

X-Ray and Electron Optics Laboratory

Professor R. E. Ogilvie, Faculty Supervisor
Professor T. O. Ziebold, Faculty Supervisor

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 for which this instrument is well suited include analysis of diffusion couples, distribution of elements in areas of dendritic segregation, identification of inclusions, and the analysis of thin films.

The laboratory has a scanning electron microscope which is available to the members of the Institute. This instrument is not only well suited for the study of irregular or fractured surfaces, but has been applied to the examination of biological materials, and conventional metallurgical polished specimens. We have just installed a non-dispersive solid state X-ray detector for qualatative analysis of inclusions and precipitates.

With this system we hope to be able to analyze sub micron areas.

The work performed in this laboratory will be carried out by one of the laboratory technicians. In special cases, graduate students under the supervision of one of the laboratory employees will be able to use the equipment on his own.

X-ray and Low-Energy Electron Diffraction Laboratory

Professor D. P. Shoemaker, Faculty Supervisor

A General Electric XRD-5 X-ray generator 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. Usage of this facility has been mainly by Professor Shoemaker's research group.

The laboratory also has a Varian Low-Energy Electron Diffraction Unit, complete with test chamber, vacuum system, bakeout over, and all needed gauges and controls. Also available is a partial pressure analyzer, and soon to be installed is an attachment for Auger spectroscopy. This equipment can be used for study and analysis of ultra-clean surfaces of crystals and of chemisorbed layers. Usage of this facility has been mainly by Professor Shoemaker's research group, in particular by Mr. John G. Keil in his Ph. D. thesis research sufaces of II-VI semiconductor compounds. The facility has also been used in a study of Dr. Leo Feinstein and Mr. Max Taylor for Dr. Sol Gilman, NASA Electronics Research Center (Cambridge, Massachusetts), on preparation of ultra-clean platinum surfaces.

In all cases, the user of these equipments is expected to do all his own crystal preparative and manipulative work, supply needed materials, and do his own interpretation of results.

Surfaces and Interfaces Central Facility

R. M. Pelloux, Faculty Advisor
L. Sudenfield, Technician

At this time the central facility of the surfaces and interfaces phenomena group is equipped with a transmission electron microscope and

a scanning electron microscope and their supporting accessories.

The scanning electron microscope is a Stereo Scan Cambridge Instrument (Model Mark II - 1969). This unit has a maximum accelerating voltage of 30 kv, a tilting stage (tilt $\pm 45^{o}$, rotation 360°) and a resolving power of the order of 250 Angstroms. The Stereo Scan can be operated in secondary electron emission mode and in back scattered electron emission. This tool is ideally suited for fracture research because of the large depth of field and the large range of magnification. During the past months the studies of crack initiation in fatigue, of cracks in bearings, fracture of composite materials, texture of electrodeposited films have shown the versatility of the scanning microscope. This unit can also be used to study the microstructure of alloys when the phases have a marked difference in electron emission.

The transmission electron microscope is an Hitachi H 11 (model 1962) with a tilting stage ($\pm 10^{o}$) and hot and cold stages. This microscope is best suited for replica work to study microstructure and fractures surfaces. With one step or two step replicas the average resolving power is of the order of 80 Angstroms which is adequate for most work. The tilting stage allows excellent stereomicrographs to be taken at high magnification.

The facilities also include stereoviewer, stereozoom optical microscope, vacuum evaporator for the preparation of carbon replicas and coating of specimen for scanning microscopy.

The facilities are readily available to the staff of the Center and to other members of the M.I.T. Community. The work can be handled by the staff or by the customer after proper training. Time and labor are charged at a nominal fee by the Center.

Gas Analyzer Mass Spectrometer Facility

Professor J. F. Elliott, Faculty Supervisor

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 the determination of ratios of concentrations of vapor species.

D. Adler, Assist. Prof., Elec. Eng. 79
R. B. Adler, Prof., Elec. Eng. 89
A. S. Argon, Prof., Mech. Eng. 251,254,256,257
F. O. Arntz, Assit. Prof., Elec. Eng. 89
B. L. Averbach, Prof., Metal. 135
S. Backer, Prof., Mech. Eng. 267
R. F. Baddour, Prof., Chem. Eng. 319,320
G. B. Benedek, Prof., Physics 19
C. A. Berg, Assoc. Prof. Mech. Eng. 251,259
M. B. Bever, Prof., Metal. 163
J. F. Breedis, Assoc. Prof. Metal. 155
D. D. Buss, Assist. Prof. Elec. Eng. 79
J. W. Cahn, Prof. Metal. 167
L. L. Chang, Assoc. Prof. Elec. Eng. 89
R. L. Coble, Prof., Metal. 215
M. Cohen, Prof., Metal. 155
E. G. Cravalho, Assist. Prof., Mech. Eng. 309
C. K. Crawford, Assist. Prof., Elec. Eng. 130
T. G. Davis, Assist. Prof., Elec. Eng. 119
P. L. deBruyn, Prof., Metal 186
P. D. DeCicco, Assist. Prof., Physics 1
M. C. Deibert, Assist. Prof., Chem. Eng. 319
C. S. Draper, Prof., Aero and Astro; Vice-Director, Instrumentation 354
M. S. Dresselhaus, Prof., Elec. Eng. 79
J. F. Elliott, Prof., Meta. 180
D. J. Epstein, Prof., Elec. Eng. 110,119
M. Feld, Assist. Prof., Physics 67
S. M. Fleming, Instructor, Chem. Eng. 314
M. C. Flemings, Prof., Metal. 189
C. W. Garland, Prof., Chemistry 49
H. C. Gatos, Prof., Metal. 197
E. R. Gilliland, Prof., Chem. Eng. 313,325,328
N. J. Grant, Prof., Metal. 173
T. J. Greytak, Assist. Prof., Physics 29
L. W. Gruenberg, Assist. Prof., Elec. Eng. 87,209
J. W. Hafstrom, Assist. Prof., Metal. 209
A. S. Hoffman, Assoc. Prof., Chem. Eng. 314,315,325,328
W. J. Ince, Assist. Prof., Elec. Eng. 110
A. Javan, Prof., Physics 67
K. H. Johnson, Assist. Prof., Metal. 135
R. C. Jones, Assoc. Prof., Civil Eng. 272
R. Kaplow, Assoc. Prof., Metal. 135
T. B. King, Prof., Meta.l 180
W. D. Kingery, Prof., Meta. 215
C. Kingsley, Jr., Assoc. Prof., Elec. Eng. 309
N. Kurnit, Assist. Prof., Physics 67
D. Kleppner, Assoc. Prof., Physics 11
G. F. Koster, Prof., Physics 1
R. L. Kyhl, Prof., Elec. Eng. 63
B. Lax, Prof., Physics; Director, National Magnet Lab. 332
J. D. Litster, Assist. Prof., Physics 25
R. C. Lord, Prof., Chemistry 59
G. Margolis, Assist. Prof., Chem. Eng. 327
F. A. McClintock, Prof., Mech. Eng. 251
F. J. McGarry, Prof., Civil Eng. 272
A. L. McWhorter, Prof., Elec. Eng.;Division Head, Lincoln Lab. 366
J. W. Mar, Prof., Aero and Astro. 262
E. W. Merrill, Prof., Chem. Eng. 325

F. Moavenzadeh, Assoc. Prof., Civil Eng. 272
M. Modell, Assist. Prof., Chem. Eng. 314, 320
C. J. Mogab, Assist. Prof., Meta. 215
J. S. Moore, Assist. Prof., Elec. Eng. 89
J. P. Moran, Assist. Prof., Aero and Astro. 305
F. R. Morgenthaler, Prof., Elec. Eng. 110
S. C. Moss, Assoc. Prof., Metal. 135
R. E. Ogilvie, Prof., Metal. 240
R. M. Pelloux, Assoc. Prof., Metal. 173
G. W. Pratt, Prof., Elec. Eng. 79
E. Rabinowicz, Prof., Mech. Eng. 296
R. H. Rediker, Prof., Elec. Eng. 89
R. C. Reid, Prof., Chem. Eng. 326, 327
B. G. Rightmire, Prof., Mech. Eng. 296
R. M. Rose, Assoc. Prof., Metal. 209
B. H. Rosof, Assist. Prof., Metal. 180
K. C. Russell, Assoc. Prof., Metal. 167
C. N. Satterfield, Prof., Chem. Eng. 316
M. O. Scully, Assoc. Prof., Physics 4
D. J. Sellmyer, Assist. Prof., Metal. 135
S. D. Senturia, Assist. Prof., Elec. Eng. 89
D. P. Shoemaker, Prof., Chem. 54
W. J. Shack, Assist. Prof., Mech. Eng. 259
S. P. Shah, Visiting Assoc. Prof., Civil Eng. 272
C. G. Shull, Prof., Physics 14
R. J. Silbey, Assoc. Prof., Chem. 57
J. C. Slater, Institute Prof. Emeritus, Physics 1
A. Smakula, Prof., Elec. Eng. 119
A. C. Smith, Assoc. Prof., Elec. Eng. 89
J. L. Smith, Jr., Prof., Mech. Eng. 309
K. A. Smith, Assoc. Prof., Chem. Eng. 325
R. A. Smith, Prof., Physics 48
D. L. Smythe, Assist. Prof., Elec. Eng. 89
H. E. Stanley, Assist. Prof., Physics 32
R. E. Stickney, Assoc. Prof., Mech. Eng. 300
M. W. P. Strandberg, Prof., Physics 63
W. D. Syniuta, Assist. Prof., Mech. Eng. 296
A. Szoke, Assoc. Prof., Physics 67
R. D. Thornton, Assoc. Prof., Elec. Eng. 89
P. Thulen, Assist. Prof., Mech. Eng. 309
L. Trilling, Prof., Aero and Astro. 305
H. H. Uhlig, Prof., Metal. 194
D. R. Uhlmann, Assoc. Prof., Metal. 215, 234
H. Y. Wachman, Prof., Aero and Astro. 305
J. N. Walpole, Assist. Prof., Elec. Eng. 89
B. D. Wedlock, Assoc. Prof., Elec. Eng. 89
Dr. R. C. Williamson, Visiting Scientist, Physics 46
A. F. Witt, Assoc. Prof., Metal. 197
H. H. Woodson, Prof., Elec. Eng. 309
B. J. Wuensch, Assoc. Prof., Metal. 215
J. Wulff, Prof. Emeritus, Metal. 209, 262
I. V. Yannas, Prof., Mech. Eng. 267
T. O. Ziebold, Assoc. Prof., Nuclear Materials, Nuclear Eng. 245
H. J. Zimmermann, Prof., Elec. Eng.; Director, Research Laboratory of Electronics v

(continued from inside front cover)

National Institutes of Health:
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Department of Transportation:
C-85-65 Northeast Corridor Transportation Project (Thornton, McGarry, Jones, Moavenzadeh).
Department of Commerce, National Bureau of Standards:
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6 6-17-70