

Research in Materials 1968-1969
Massachusetts Institute of Technology

The MIT Press
Massachusetts Institute of Technology
Cambridge, Massachusetts 02142
M.I.T. Report No. 18

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

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 agencies of the United States Government as follows:

Department of Defense:

Advanced Research Projects Agency:

SD-90 (Center for Materials Science and Engineering: D. Adler, R. B. Adler, Argon, Arntz, Averbach, Benedek, Berg, Breedis, Cahn, DeCicco, Dresselhaus, Elliott, Epstein, Flemings, Garland, Gatos, Grant, Greytak, Gruenberg, Guernsey, K. H. Johnson, Jones, Kaplow, Kleppner, Litster, McGarry, Moore, Morgenthaler, Moss, Ogilvie, Pratt, Rediker, Rose, Russell, Scully, Sellmyer, Shoemaker, Smakula, Thornton, Uhlman, Williamson, Witt, Wulff, Ziebold).

Department of the Army:

DA-28-043-AMC-01978 (E) (Gray, Wedlock Smythe); DA-28-043-AMC-02536 (E) (Research Laboratory of Electronics, supported in part by the Joint Services Electronic Program; Garland, Kleppner, Kyhl, Perry, Stickney, Strandberg); DA-31-124-ARO(D)-47 (Uhlrig); DA-31-124-ARO(D)-92 (Pratt); DA-31-124-ARO(D)-187 (deBruyn); DA-31-124-ARO(D)-328 (Grant); DA-31-124-ARO(D)-358 (Shoemaker); DA-31-124-ARO(D)-425 (Greytak, Litster, Benedek); DA-36-038-AMC-2943(A) (Flemings); DA-44-009-AMC-117(T) (Smakula); DA-AMC-18-035-76(A) (deBruyn); DAHC 04-07-C-0036 (Elliott); DAHC 04-68-C-0022 (Javan, Szoke, Feld); DAAG-46-68-C-0043 (Flemings); DAAG-46-68-C-004 (Flemings).

Department of the Navy:

N00014-67-A-0204-0005 (Slater, Koster, DeCicco); N00014-67-A-0204-0006 (Kleppner); N00014-67-A-0204-0010 (Rediker, Walpole, Moore); N00014-67-A-0204-0013 (Ziebold); N00014-67-A-0204-0014 (Javan, Szoke, Feld); N00014-67-A-0204-0025 (Smakula); N00019-67-C-0500 (Grant); N00030-68-C-0154 (Instrumentation Lab); N00030-66-C-0189 (Instrumentation Lab); Nonr-1841(17) (Averbach, Kaplow); Nonr-1841(32) (Ogilvie); Nonr-1841(34) (Slater, Koster, DeCicco); Nonr-1841(35) (Cohen, Kaplow, Cahn); Nonr-1841(48) (Kaplow); Nonr-1841(51) (R. B. Adler, A. C. Smith, Senturia); Nonr-1841(72) (Pratt, D. Adler); Nonr-3963(05) (Gatos, Witt); Nonr-3963(09) (Flemings); Nonr-3963(16) (Rose Gruenberg); Nonr-3963(18) (Grant); Nonr-3963(19) (Bever); Nonr-3963(20) (Smakula); Nonr-3963(22) (Javan, Szoke, Feld); Nonr-4102(01) (Project MAC, Kaplow); NR 018-106 (Pratt, D. Adler, Dresselhaus).

Department of the Air Force:

AF 04(694)-999 (Instrumentation Laboratory); F19(268)-67-C-0074 (Javan, Szoke, Feld); AF 19(628)-5167 (Lincoln Laboratory, also Gatos, J. L. Smith, Jr.); AF 19(628)-5876 (Morgenthaler); AF 19(628)-6066 (Perry); AF 33(615)-2712 (McGarry); AF 33(615)-3866 (Breedis); F33615-68-C-1020 (Crawford); F33615-67-C-1226 (Averbach, Kaplow); F33615-67-C-1441 (Grant); AF 33(615)-3395 (Epstein); F44620-67-C-0047 (National Magnet Laboratory); AF 49(638)-1463 (Wulff, Mar); AFOSR 68-1571 (Rediker); F19 (268)-68-C-0204 (Javan, Feld, Szoke); F33615-69-C-1031 (Gatos, Witt); F33615-68-C-1155 (Instrumentation Laboratory); F33615-68-C-1490 (Smakula).

National Aeronautics and Space Administration:

NAS9-4065 (Instrumentation Laboratory); NAS9-4576 (Instrumentation Laboratory); NAS12-569 (Instrumentation Laboratory); NAS12-679 (Crawford); NAS12-2040 (Sellmyer); NGL-22-009-012 (Javan, Szoke, Feld); NGR-22-009-091 (Stickney); NGR-22-009-125 (Gatos, Witt); NGR-22-009-182 (Benedek, Litster, Greytak); NGR-22-009-237 (Perry); NGR-22-009-240 (Javan, Szoke, Feld); NGR-22-009-247 (Kleppner); NGR-22-009-249 (Benedek); NSG-117-61 (Grant); NSG-496 part (Center for Space Research, also Bever, Gatos, Ogilvie, Rediker, Satterfield, Witt, Ziebold).

Atomic Energy Commission:

AT(30-1)-1002 (Bever); AT(30-1)-3031 (Shull); AT(30-1)-3773 (Wuensch, Uhlmann, Coble, Kingery, Mogab); AT(30-1)-3911 (Instrumentation Laboratory); AT(38-1)-334 (Mason); W-7405-ENG-48 (Lawrence Radiation Laboratory Purchase Order) (Gilliland, Hoffman).

National Science Foundation:

GA-1549 (Wuensch); GK-596 (Argon); GK-754 (Elliott); GK-1020 (Reid); GK-1071 (Wulff, Rose); GK-1073 (Wulff, Rose); GK-1034 (Cahn, Russell); GK-1374 (Grant); GK-1653 (Gatos, Witt); GK-1688X (Rose, Wulff); GK-1699X (Baddour, Deibert); GK-1707 (Satterfield); GK-1768 (Ziebold); GK-1875X (McClintock); GK-1947 (Averbach, Kaplow); GK-2024 (Yannas); GK-2911 (Wulff, Rose); GK-3686 (J. L. Smith, Jr.); GK-3700 (Argon); GP-3241 (Slater, Koster, DeCicco); GP-4923X2 (Lord, Perry); GP-4977 (Shoemaker); GP-5042 (Garland); GP-5463 (Averbach); GP-6195 (Shull); GP-7677 (Slater, Koster, DeCicco); GP-8303 (Shull); GP-8387 (Silbey).

(continued on inside back cover)

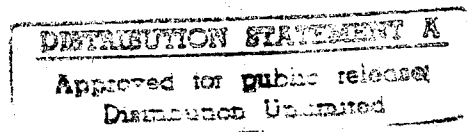
ANNUAL REPORT 1968 - 1969

RESEARCH IN MATERIALS

MASSACHUSETTS
INSTITUTE OF TECHNOLOGY

CAMBRIDGE, MASSACHUSETTS

APRIL 1969



19960503 101

DTIC QUALITY INSPECTED 1

7500

750-72



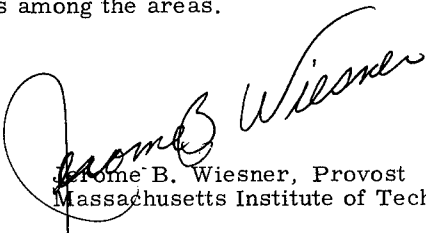
OFFICE OF THE PROVOST

CAMBRIDGE, MASSACHUSETTS 02139

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

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

Materials science and engineering activities are an important aspect of the teaching and research programs in many departments of the School of 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.


Jerome B. Wiesner, Provost
Massachusetts Institute of Technology

March 1969

INTRODUCTION

This is the eighth 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 Interdisciplinary Laboratory Building of the Center for Materials 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 their 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 primarily intended 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. There is, for example, the high magnetic field facility in the National Magnet Laboratory; there is the Spectroscopy Laboratory, directed by Professor R. C. Lord of the Department of Chemistry, which provides a wealth of spectroscopic experience as well as excellent facilities. The Cryogenic Laboratory in the Department of Mechanical Engineering under Professor J. L. Smith provides advice and coolants for low temperature work. The structuring of the several Central Facilities for materials preparation and evaluation, which was established in the Center for Materials Science and Engineering through ARPA support, permits 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 facilities are available on an Institute-wide basis.

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 listed in the text. 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 1969

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, Asst. Professor, Physics	
II. Non-Equilibrium Quantum Statistical Mechanics	5
M. Scully, Asst. Professor, Physics	
III. Atomic Resonance and Scattering	12
D. Kleppner, Assoc. Professor, Physics	
IV. Neutron Diffraction and Neutron Physics Studies	15
C. G. Shull, Professor, Physics	
V. The Spectroscopy of Light Scattered from Thermal Fluctuations in Liquids, Solids, and Gases	21
G. B. Benedek, Professor, Physics	
VI. Optical Spectroscopy of Magnetic Solids Near the Critical Point	27
J. D. Litster, Asst. Professor, Physics	
VII. Light Scattered from Excitations in Helium ⁴ and Helium ³ -Helium ⁴ Mixtures	30
T. J. Greytak, Asst. Professor, Physics	
VIII. Order-Disorder Phenomena	33
C. W. Garland, Professor, Chemistry	
IX. Crystal and Surface Structure Investigations by X-ray, Neutron and Electron Diffraction	40
D. P. Shoemaker, Professor, Chemistry	
X. Molecular Crystals	43
R. J. Silbey, Asst. Professor, Chemistry	
XI. Molecular Spectroscopy	45
R. C. Lord, Professor, Chemistry	
XII. Infrared and Raman Spectroscopy of Solids	49
C. H. Perry, Asst. Professor, Physics	
XIII. Microwave Spectroscopy	56
M. W. P. Strandberg, Professor, Physics	
R. L. Kyle, Professor, Electrical Engineering	
XIV. Optical and Infrared Masers	61
A. Javan, Professor, Physics	
A. Szoke, Assoc. Professor, Physics	
M. Feld, Asst. Professor, Physics	
R. Brewer, Visiting Professor, Physics	
G. Koppelman, Visiting Assoc. Professor, Physics	

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

I. Solid State Study Group	73
G. W. Pratt, Jr., Professor, Electrical Engineering	
M. S. Dresselhaus, Professor, Electrical Engineering	
D. Adler, Asst. Professor, Electrical Engineering	
D. D. Buss, Asst. Professor, Electrical Engineering	
II. Superconductivity Theory	80
L. W. Gruenberg, Asst. Professor, Electrical Engineering	
III. Semiconductor Materials and Devices	82
R. B. Adler, Professor, Electrical Engineering	
R. H. Rediker, Professor, Electrical Engineering	
P. E. Gray, 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, Asst. Professor, Electrical Engineering	
J. S. Moore, Asst. Professor, Electrical Engineering	
S. D. Senturia, Asst. Professor, Electrical Engineering	
D. L. Smythe, Asst. Professor, Electrical Engineering	
J. N. Walpole, Asst. Professor, Electrical Engineering	
IV. Microwave and Quantum Magnetics	105
D. J. Esptein, Professor, Electrical Engineering	
F. R. Morgenthaler, Professor, Electrical Engineering	
R. Nevald, Visiting Asst. Professor, Electrical Engineering	
V. Crystals Physics Laboratory	112
A. Smakula, Professor, Electrical Engineering	
VI. Particle Optics Laboratory	129
C. K. Crawford, Asst. Professor, Electrical Engineering	

SECTION C. METALLURGY AND MATERIALS SCIENCE

I. Physics of Solids	133
B. L. Averbach, Professor, Metallurgy and Mats. Sci.	
R. Kaplow, Assoc. Professor, Metallurgy and Mats. Sci.	
S. C. Moss, Assoc. Professor, Metallurgy and Mats. Sci.	
D. J. Sellmyer, Asst. Professor, Metallurgy and Mats. Sci.	
K. H. Johnson, Asst. Professor, Metallurgy and Mats. Sci.	
II. Physical Metallurgy	154
M. Cohen, Ford Professor of Metallurgy and Mats. Sci.	
J. F. Breedis, Assoc. Professor, Metallurgy and Mats. Sci.	
III. Physical Metallurgy	161
M. B. Bever, Professor, Metallurgy and Mats. Sci.	
IV. Physical Metallurgy	167
J. W. Cahn, Professor, Metallurgy and Mats. Sci.	
K. C. Russell, Asst. Professor, Metallurgy and Mats. Sci.	
V. High Temperature Metallurgy	172
N. J. Grant, Professor, Metallurgy and Mats. Sci.	
VI. Process Metallurgy and High Temperature Chemistry	180
J. F. Elliott, Professor, Metallurgy and Mats. Sci.	
T. B. King, Professor, Metallurgy and Mats. Sci.	
B. H. Rosof, Asst. Professor, Metallurgy and Mats. Sci.	
VII. Surface Chemistry	185
P. L. deBruyn, Professor, Metallurgy and Mats. Sci.	
VIII. Metals Processing - Casting and Solidification	188
M. C. Flemings, Assoc. Professor, Metallurgy and Mats. Sci.	
IX. Corrosion Laboratory	194
H. H. Uhlig, Professor, Metallurgy and Mats. Sci.	

X. Electronic Materials Laboratory	197
H. C. Gatos, Professor, Metallurgy and Mats. Sci.	
A. F. Witt, Assoc. Professor, Metallurgy and Mats. Sci.	
XI. Superconductive Materials	207
J. Wulff, Professor Emeritus, Metallurgy and Mats. Sci.	
R. M. Rose, Assoc. Professor, Metallurgy and Mats. Sci.	
L. W. Gruenberg, Assoc. Professor, Electrical Engineering	
XII. Ceramics	213
R. L. Coble, Assoc. Professor, Metallurgy and Mats. Sci.	
W. D. Kingery, Professor, Metallurgy and Mats. Sci.	
C. J. Mogab, Asst. Professor, Metallurgy and Mats. Sci.	
D. R. Uhlmann, Asst. Professor, Metallurgy and Mats. Sci.	
B. J. Wuensch, Asst. Professor, Metallurgy and Mats. Sci.	
XIII. Polymers and Glasses	238
D. R. Uhlmann, Asst. Professor, Metallurgy and Mats. Sci.	
XIV. X-ray and Electron Optics Laboratory	241
R. E. Ogilvie, Professor, Metallurgy and Mats. Sci.	
XV. Nuclear Materials Laboratory	244
T. O. Ziebold, Assoc. Professor of Nuclear Mats., Nuc. Eng.	
 SECTION D. MATERIALS ENGINEERING	
I. Mechanics of Ductile Fracture	249
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	252
A. S. Argon, Professor, Mechanical Engineering	
III. Mechanisms of Fatigue Damage in Semi-Brittle Materials at Elevated Temperatures	254
A. S. Argon, Professor, Mechanical Engineering	
IV. Mechanics and Physics of Damage in Heterogeneous Materials	257
C. A. Berg, Assoc. Professor, Mechanical Engineering	
V. Properties of Fiber Composites	259
J. Wulff, Professor Emeritus, Metallurgy and Mats. Sci.	
J. W. Mar, Professor, Aeronautical and Astronautical	
VI. Physical and Chemical Properties of Fibers and Polymers	261
S. Backer, Professor, Mechanical Engineering	
I. V. Yannas, Asst. Professor, Mechanical Engineering	
E. S. Gilfillan, Visiting Professor, Mechanical Engineering	
VII. Structural Materials	267
F. J. McGarry, Professor, Civil Engineering	
R. C. Jones, Assoc. Professor, Civil Engineering	
F. Moavenzadeh, Assoc. Professor, Civil Engineering	
R. B. Williamson, Asst. Professor, Civil Engineering	
VIII. Surface Properties and Behavior of Materials	284
B. G. Rightmire, Professor, Mechanical Engineering	
E. Rabinowitz, Professor, Mechanical Engineering	
W. D. Syniuta, Asst. Professor, Mechanical Engineering	
IX. Surface Properties and Processes	288
R. E. Stickney, Assoc. Professor, Mechanical Engineering	
X. Cryogenic Engineering Laboratory	293
J. L. Smith, Jr., Assoc. Professor, Mechanical Engineering	
J. Gerstmann, Asst. Professor, Mechanical Engineering	
E. G. Cravalho, Asst. Professor, Mechanical Engineering	
XI. Chemical Engineering of Materials	297
1.0 Properties of Complex Coacervates of Polyelectrolytes	297
A. S. Hoffman, Assoc. Professor, Chem. Engineering	
2.0 Reverse Osmosis Desalination Membranes	297
A. S. Hoffman, Assoc. Professor, Chem. Engineering	
M. Modell, Asst. Professor, Chem. Engineering	

3.0	Catalysis	298
3.1	Interphase Electronic Interactions in Polyphase Solid Catalysts	298
	R. F. Baddour, Professor, Chem. Engineering	
	M. C. Deibert, Asst. Professor, Chem. Engineering	
3.2	Heterogeneous Catalysis	299
	R. F. Baddour, Professor, Chem. Engineering	
	M. Modell, Asst. Professor, Chem. Engineering	
4.0	Biomaterials	301
4.1	Non-Thrombogenic Polymers, and Aerosol Surfactants for Pulmonary Therapy	301
	E. W. Merrill, Professor, Chem. Engineering	
	K. A. Smith, Assoc. Professor, Chem. Engineering	
	E. R. Gilliland, Professor, Chem. Engineering	
4.2	Structure and Properties of Elastin	303
	A. S. Hoffman, Assoc. Professor, Chem. Engineering	
5.0	Cryogenic Chemistry	303
	R. C. Reid, Professor, Chem. Engineering	
	M. W. P. Strandberg, Professor, Physics	
6.0	Diffusion and Reaction in Porous Materials	304
	C. N. Satterfield, Professor, Chem. Engineering	
XII.	Effects of Radiation on Materials	307
1.0	Effects of Radiation on Organic Coolants for Nuclear Reactors	307
	E. A. Mason, Professor, Nuclear Engineering	
2.0	Radiation Acceleration of Viscoelastic Processes in Polymers	310
	E. R. Gilliland, Professor, Chem. Engineering	
	A. S. Hoffman, Assoc. Professor, Chem. Engineering	

SECTION E. FRANCIS BITTER NATIONAL MAGNET LABORATORY

1.0	High Field Magnet Development	315
2.0	Magnetic Proof-loading of Aircraft Structures	316
3.0	Magnetic Ore Separation	317
4.0	Medical Magnet Project	318
5.0	Limiting Effects in High Field Superconductors	319
6.0	Exchange Enhancement in Metals and Alloys	320
7.0	Transport Studies of Local Moments in Dilute Alloys	321
8.0	Magnetism in Nearly Ferromagnetic Metals and Alloys	321
9.0	Magnetic Properties of Rare-Earth Single Crystals	322
10.0	High Temperature Superconductors	322
11.0	High Field Resonance in Cerous Magnesium Nitrate	323
12.0	Mossbauer Effect Studies	324
12.1	Metals and Alloys	324
12.2	Non-metals	325
13.0	Laser Spectroscopy	325
13.1	Multiphoton Interband Absorption in Semiconductors	325
13.2	Luminescence Studies	326
14.0	Magneto-Plasma-Phonon Interactions in Solids	326
15.0	Submillimeter Cyclotron Resonance	326
16.0	Infrared Magnetospectroscopy	327
16.1	Reflection and Electoreflexion Studies of Interband Magneto-Optical Transitions in Semiconductors	327
16.2	Magnetopiezo-optical Studies of Germanium and the Lead Salts	328
16.3	Energy Band Studies in Uniaxially Stressed Semiconductors	329
17.0	Adiabatic Demagnetization	329
18.0	Ionic Mobility in ³ He in Magnetic Fields	330

19.0	Fluctuation Phenomena in Thin Film Superconductors	330
20.0	Resonance Studies in Dilute Alloys	331
21.0	Cyclotron Resonance in Single Crystal Graphite	332
22.0	Ultrasonic Studies	332
23.0	High Field Superconductivity in V_3Ga and V_3Si	333
24.0	Piezo-Magnetoresistance in Degenerate Semiconductors	334
25.0	Quantum Limit Transport Phenomena	334
26.0	Spin Wave Side Bands	335
27.0	Calculation of the Magnetic Susceptibility of Pd	335
28.0	Magnetic Measurements Employing an AC Temperature Technique	336
28.1	$\partial M/\partial T$ Measurements in Paramagnetic Pd-Fe Alloys	336
28.2	Spin Waves in Dilute Ferromagnetic Alloys	336
29.0	Theory of Electron Interaction in Magnetic Metals	337
30.0	Neutron Scattering in Ferromagnetic Dilute Alloys	338
31.0	Ultra-High Critical Field in Superconductors with Magnetic Impurities	339
32.0	The Dynamics of Electrons in Solids in External Fields	340
33.0	Instrumentation for High Magnetic Field Research	341
33.1	Low Temperature Thermometry in Magnetic Fields	341
33.2	Improved Techniques for Detecting Low Light Levels	342
34.0	Kinetic Inductance Measurements of Linear Superconductors	343
35.0	Calorimetric Measurements Employing an AC Temperature Technique	343
36.0	Cooperative Programs	344

SECTION F. INSTRUMENTATION LABORATORY

1.0	Fracture Mechanisms in Oceanic Cable	349
2.0	Synthesis of High Density Gyro Fluids	349
3.0	Studies of Materials for Gas-Lubricated Gyro Bearings	350
4.0	Newtonian Behavior of Damping Fluids	350
5.0	Permanent Magnet Stability	351
6.0	Disaccommodation in Ferrites	352
7.0	Analysis of Contamination in Gyroscopes by Electron Beam Micro-Analysis	352
8.0	Investigation of Gyro Damping Fluids by Gel Permeation Chromatography; A Study of the Correlation between GPC and Thermal Diffusion	353
9.0	Accelerometer Fluids	354
10.0	Gyro Damping Fluids	355
11.0	Determination of the Unsaturation in Damping Fluids Using the Technique of Microhydrogenation	355
12.0	Damping Fluid Properties at Low Temperatures	356
13.0	Determination of Coefficient of Thermal Expansion	357
14.0	Brazing Difficult-to-Join Materials	357

SECTION G. LINCOLN LABORATORY

1.0	Solid State Theory	361
2.0	Electronic Materials	364
3.0	Solid State Physics	368
3.1	Band Structure	369
3.2	Magnetic Interactions and Ordering	370
3.3	Scattering Experiments with Lasers	370
4.0	Applied Physics	373
5.0	Computer Components (Data Systems Division)	378
5.1	Magnetic Films	378
5.2	Materials for Memory Applications	379

5.3. Hot Electron Transport in Metals	380
INDEX - FACULTY	383

CHEMICAL AND SOLID STATE PHYSICS

I. SOLID STATE AND MOLECULAR THEORY GROUP

Faculty:

J. C. Slater, Institute Professor, Emeritus, Physics
G. F. Koster, Professor, Physics
P. D. DeCicco, Assistant Professor, Physics

Research Staff and Graduate Students:

D. Becker, Physics
J. W. Gadzuk, Mechanical Engineering
R. Gilmore, Instructor, Physics
D. Klingspon, Physics
D. Koelling, Physics
B. Mayes, Physics
W. Rudge, Physics
Josephine Shea, Materials Science Center, Secretary

Personnel who have left:

D. Becker
J. W. Gadzuk
D. Koelling
W. Rudge

Degrees Granted:

D. Becker, Ph.D., Physics, September 1968
J. W. Gadzuk, Ph.D., Mechanical Engineering, February 1968
D. Koelling, Ph.D., Physics, September 1968
W. Rudge, Ph.D., Physics, September 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75106
Office of Naval Research, Nonr-1841(34), DSR 75251
National Science Foundation, NSF-GP-3241, DSR 77648
Office of Naval Research, N00014-67-A-0204-0005, DSR 70280
National Science Foundation, NSF-GP-7677, DSR 70607

Research Report

As in preceding ARPA Reports, we indicate the fields of interest of the members of the group by indicating the titles of the contributions to the four Quarterly Progress Reports issued during the year, namely Reports Nos. 67, 68, 69, and 70, issued on January 15, April 15, July 15, and October 15, 1968, respectively.

Contents of Quarterly Progress Reports Nos. 67, 68, 69, and 70:

- P. DeCicco, Hartree-Fock VS. Local-Potential Energy Bands in KCL, 67.
- J. W. Gadzuk, The Theory of Velocity Distributions of Atoms Evaporating from Liquid Helium II, 68.
- J. W. Gadzuk, Dielectric Formulation of Many-Body Effects at Electron Gas Surfaces, 68.
- R. Gilmore, Irreducible Representations of the Simple Lie Groups, 69.
- R. Gilmore, Construction of Weight Spaces for Irreducible Representations of A_n , B_n , C_n , D_n , 70.
- K. H. Johnson, Molecular Model for the Localized Electronic Structure of Imperfections in Crystals, 67.
- K. H. Johnson, J. Connolly, The Localized Electronic Structure of Crystal Imperfections. II. The Bound States of Surface and Line Defects, 70.
- K. H. Johnson, The Electronic Structure of Cesium Chloride Type Intermetallic Compounds, 70.
- D. Koelling, Exchange Potentials in Gadolinium: A Preliminary Report, 67.
- D. Koelling, The Relativistic APW Method and Its Convergence in l , 68.
- D. Koelling, The Hexagonal Close Packed Double Space Group (D_{6h}^4) Representations, 68.
- D. Koelling, Space Group Representations for Diamond: An Erratum, 68.
- E. Lafon, Charge Density of Diamond by the Method of Tight Binding, 69.
- B. Mayes, Inelastic Collisions of Electrons with Argone which Excite the $3p^5 4s$ Configuration.
- W. E. Rudge, Crystalline Coulomb Potential Energy, 67.
- W. E. Rudge, Non-Muffin Tin APW Matrix Elements and Charge Density for Monatomic Cubic Crystals, 68.
- W. E. Rudge, Generalized Ewald Potential Problem, 68.
- W. E. Rudge, Self-Consistent APW Calculations for Lithium, 69.
- M. O. Scully, F. Hopf, Theory of an Inhomogeneously Broadened Laser Amplifier, 70.
- J. C. Slater, T. M. Wilson, J. H. Wood, Non-Integral Occupation Numbers in Transition Atoms, 69.

Publications

- D. S. Becker, Theoretical Determination of Fermi Surfaces of Cubic Metals by a Modification of the Augmented Plane Wave Method, M. I. T. Thesis, 1968.
- P. D. DeCicco and A. Kitz, Calculation of Neutron and X-Ray Scattering Amplitudes for bcc Iron, Phys. Rev. 162, 486 (1967).
- J. W. Gadzuk, Screening of a Point Impurity in the Surface Region of an Electron Gas, Solid State Comm. , 5, 743 (1967).
- J. W. Gadzuk, Many-Body Theory of a Rapidly Varying Inhomogeneous Electron Gas, M. I. T. Thesis, 1968.
- J. W. Gadzuk, The Effects of Screened Exchange and Correlation of the Surface Potential of an Electron Gas, Surface Sci. , 11, 465 (1968).
- J. W. Gadzuk, Theory of Velocity Distributions of Atoms Evaporating from Liquid Helium II. , Phys. Letters, 27a, 23 (1968).
- J. W. Gadzuk, Theory of Metallic Absorption of Real Metal Surfaces, Presented at 4th International Materials Symposium, "The Structure and Chemistry of Solid Surfaces", Berkely, Calif. , June 1968.
- D. Koelling, The Augmented Plane Wave Method Applied to Tin, M. I. T. Thesis, 1968.
- B. W. Mayes, Inelastic Collisions of Electrons with Atoms, M. I. T. Thesis, 1968.
- W. E. Rudge, A Self-Consistent Augmented Plane Wave Calculation of Energy Bands in Lithium, M. I. T. Thesis, 1968.
- J. C. Slater, The Current State of Solid-State and Molecular Theory, Int. J. Quant. Chem. 1, 37-102 (1967).
- J. C. Slater, Quantum Physics in America Between the Wars, Int. J. Quant. Chem. 1S, 1-23 (1967).
- J. C. Slater, Energy Bands and Fermi Surfaces, Int. J. Quant. Chem. 1S , 523-531 (1967).
- J. C. Slater, Correlation Problems in Solids, Int. J. Quant. Chem. 1S , 783-789 (1967).
- J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 3 , Insulators Semiconductors, and Metals, McGraw-hill Book Co. , New York, 1967.
- J. C. Slater, Introduction to the Theory of Ferroelectricity, from "Ferroelectricity", Elsevier Pub. Co. , Amsterdam-London-New York, 1967, pp. 1-8.
- J. C. Slater, Review of "Second Quantization and Atomic Spectroscopy", by Brian R. Judd, Am. J. Phys. 36 , 69 (1968).

- J. C. Slater, Energy-Band Theory of Magnetism, J. Appl. Phys. 39 , 761-767 (1968).
- J. C. Slater, Average Energy of States of Given Multiplicities in Atoms, Phys. Rev. 165 , 655-658 (1968).
- J. C. Slater, Exchange in Spin-Polarized Energy Bands, Phys. Rev. 165 , 658-669 (1968).
- J. C. Slater, Quantum Physics in America Between the Wars, Physics Today 21 , 43-51 (January 1968).
- J. C. Slater, Energy Bands in Solids, Physics Today 21 , 61-71 (April 1968).
- J. C. Slater, Quantum Theory of Matter , 2d edition, McGraw-Hill Book Co. , New York, 1968
- J. Sokoloff, Some Consequences of the Thermal Hartree-Fock Approximation at Zero Temperature, Annals of Physics 45, November 1967.

II. NON-EQUILIBRIUM QUANTUM STATISTICAL MECHANICS

Faculty:

M. Scully, Assistant Professor, Physics

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

N. Lee, Graduate Fellow, Physics

P. Lee, Research Assistant, Physics

J. Blinkship, Senior Student, Physics

C. Eng, Senior Student, Physics

D. Limbert, Senior Student, Physics

J. Stewart, Senior Student, Physics

S. Nagel, Undergraduate Assistant, Physics

Degrees Granted:

F. Hopf, Ph.D., Physics, Yale University, June 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75105

Research Report

1.0 Quantum Theory of Laser Behavior^{1, 2}

Personnel: M. Scully; D. Kim, R. Lang

1.1 General

With the advent of the laser a new dimension was added to the subject of optical coherence. It was no longer possible to completely characterize the degree of coherence of an optical source by simply specifying its degree of mono-chromaticity. In order to properly understand the coherence of laser radiation one must quantize electromagnetic field and obtain an equation of motion for the laser radiation density matrix as it evolves under the influence of a nonthermal reservoir representing the lasing medium and a thermal reservoir representing the effects of cavity losses. It is then clear that the complete theory of laser behavior is basically a problem in nonequilibrium quantum statistical mechanics. Such a theory¹ was developed in collaboration with Prof. W. E. Lamb and is being extended in the following directions.

1.2 Theory of Related Measurements^{3,4}

In order to relate the results of this analysis to experimentally measurable quantities the theory was extended to include a quantum mechanical analysis of a spectrum analyzer and photodetector.

1.3 Generalizations^{5,6} to Include Frequency Pulling, Temperature Effects, etc.

The general theory has been extended to include the effects of atomic motion and recoil and the frequency of laser oscillation as a functional of temperature and detuning.

1.4 Super-radiance in Laser Operations

The purpose of this research is to incorporate into the theory of a laser oscillator the collective aspects of the lasing atoms. This calls for a rather involved treatment of the many body effects in a laser theory. To this end we start from the observation that the two level atoms can be profitably compared to a spin 1/2 system and thus use the angular momentum formalism developed by Dicke. A system of equations describing the evolution of the composite system of atoms and radiation has been developed. Progress is being made on this problem.

2.0 Coherence⁷ and the Interaction of Radiation with Matter

Personnel: M. Scully; I. Asher, H. Auvermann, F. Hopf

2.1 Amplification of Ultra Short Pulses (theory)⁸

Recent advances in laser technology have led to the production of ultra-short electromagnetic pulses of very high peak power. In the past year we have developed a theory which describes the transient behavior of such pulses in a laser amplifier. The effects of atomic coherence and inhomogeneous broadening, necessary for a complete treatment of the problem are included. The two level active atoms are characterized by a phase memory time T_2 and an inhomogeneous frequency distribution (which leads to a reversible decay time T_2^*). The field (Maxwell) and atomic (Schrodinger) equations are coupled in a self-consistent manner. The resulting equations are solved analytically in certain limits while the general case is integrated numerically. The emphasis is placed on the situation in which T_2^* and the pulse width are much shorter than T_2 . Thus our main effort is devoted to the physics of the inhomogeneously broadened system. The theory itself, however, contains the effects of both forms of broadening. The basic difference between the inhomogeneous and homogeneous broadening is discussed. In the former case, the decay of radiation is caused by the dephasing of dipoles, and is reversible. The atomic memory is retained during the dephasing, and an internal reflection of the atomic coordinates, as is exemplified in the "photon echo" process, will cause the dipoles to rephase. The phonon interruptions or atomic collisions that bring about the homogeneous broadening are random processes which lead to an irreversible destruction of the atomic phase memory. The implications of the reversible vs. irreversible decay processes are seen to have important consequences in the problem of pulse amplification. The possibility of using the ultrashort pulses as a new means of studying materials is pointed out.

2.2 Amplification of Ultras Short Pulses (experiment)

In conjunction with the NASA Cambridge group, experiments are being assembled in order to check the predictions of the theory. We propose to carry out experiments at liquid helium and nitrogen as well as room temperatures. These measurements should indicate the extent to which the coherent atomic transitions enhance the amplification process, and provide a new means of measuring atomic memory times as well as the width of the inhomogeneous broadening.

2.3 Photon Echo⁹

In other work we have investigated the possibility of observing "photon

echo" in gases, in order to determine the conditions under which an echo would be expected. The results are similar to those obtained in a solid, except that the time between exciting pulses is limited when the two pulses do not travel in the same direction. With increasing pulse separation collisions reduce the echo intensity in a way which is characteristic of the type of collision process.

2.4 Mode Locking

Study has begun on the interaction of lasing modes having different polarizations. The simplest case is two modes with perpendicular electric vectors. Population competition effects will be analyzed in the third order perturbation theory and the resulting mode locking investigated. Atomic motion will be included.

3.0 Coherence in Superfluid Systems

Personnel: M. Scully; C. Boley, P. Lee

3.1 Josephson Radiation¹⁰

Considerable experimental activity has been directed toward measuring the ratio of the electronic charge to Planck's constant. The basis for these measurements is the observation that when a pair tunnels between two superconductors maintained at a potential difference V , a photon is emitted having a frequency $\omega = 2eV/\hbar$. In a recent communication we derive a shift in the frequency of the emitted radiation due to cavity pulling effects, using techniques developed in the theory of laser oscillators.

In our model we consider the junction to be at absolute zero and to consist of two films of identical material separated by a thin oxide barrier. When pairs tunnel across the barrier they excite a single mode of the electromagnetic field having an eigenfrequency Ω and a bandwidth $\Delta\omega = \nu/Q$. In order to maintain charge neutrality pairs must be removed from one side of the barrier and added to the other by means of an external circuit.

We treat the problem as an exercise in nonequilibrium statistical mechanics in analogy with the quantum theory of the laser. The radiation-superconductor system is coupled to reservoirs which represent the effects of a finite cavity Q in the case of the field while in the case of the superconductors the reservoirs represent the wires (of normal metal) which are necessary in order to maintain charge neutrality. After demonstrating the frequency pulling effect, a simple physical argument is given which leads to the same result. An experiment is suggested which would measure the frequency pulling effect.

3.2 Liquid Helium

Stimulated by recent experimental investigations carried out in the MIT group of Prof. J. King we have started to study some nonequilibrium processes which occur in liquid helium. For this purpose we are extending techniques which have already been applied to lasers and superconductors. These techniques are useful for describing composite systems, in situations when one is interested only in a particular subsystem and is content to average over the behavior of the other subsystems. Two problems are being considered. In the first, we have introduced a coupling between HeII atoms and a temperature reservoir, and have investigated the time-dependence of the average number of zero-momentum particles. In the second problem we are concerned with the evaporation of helium atoms from the superfluid. We plan to study the velocity distribution of particles in the vapor as well as correlations in the evaporation process. Our method is to treat the problem in terms of tunneling, with the surface providing the barrier. Since only the vapor is of interest, we may trace over the state of the liquid.

4.0 Phonons

Personnel: M. Scully; I. Asher, J. Goldstein, N. Lee

4.1 Acoustoelectric Amplification - a phonon maser

The amplification of acoustic waves in a piezoelectric semiconductor as first elucidated by White, has been an area of considerable interest in modern solid-state physics.

In practice, one applies a DC electric field to a rod made of CdS or some other piezoelectric material. This displaces the Fermi distribution of the electrons in velocity space. An acoustic wave is then propagated along the direction of the DC field. Those electrons with velocities greater than that of the sound wave, can make transitions to lower velocity states, by emitting phonons to the acoustic field. This process is enhanced by the piezoelectric coupling between the phonons (lattice wave) and the AC electric field due to electron bunching. As Pippard points out, this process is not unlike the stimulated emission of photons in the laser case.

We envisage this acoustoelectric interaction in terms of a self-consistent calculation, similar in technique to Lamb's classical theory of the laser. Such a calculation would not only extend White's theory to the important non-linear region, but also elucidate the apparent analogy between the acousto-electric amplifier and a laser.

4.2 The Statistics of Radiation Scattered from Acoustical Phonons

Work has begun on the problem of finding the density matrix for laser radiation scattered from excitations such as phonons. Since the density matrix for the scattered light contains all possible knowledge concerning the scattered radiation it should enable us to deal with questions such as when the correlation function $G^{(2)}(tt')$ may be simply related to $G^{(1)}(tt')$. These studies should be of interest to the MIT group of Prof. G. Benedek and others.

5.0 On the Approach to Thermal Equilibrium and Steady State

Personnel: M. O. Scully; C. Boley, J. Stewart

5.1 A Thermodynamic Paradox

We have studied a model which involves the interaction of atoms with the radiation field. It exhibits nonequilibrium behavior, and its time development can be obtained within a reasonable approximation scheme. It was proposed by J. C. Fallows, "New Scientist" (1959) as a thermodynamic paradox, however our solution points out the fallacy in the argument. The model consists of an ellipsoid with foci at A and B. Part of a small sphere is built with center at A, and the surface within the ellipsoid-sphere structure are removed. The interior surfaces are assumed to be perfectly reflecting. At some time identical black bodies with the same temperature are placed at A and B. Because of the geometry, most of the radiation from the two sources falls on A. If A heats up and B cools down, as they might be expected to do, then the second law of thermodynamics is violated, since the systems temperature becomes progressively nonuniform. The fallacy in this argument lies in the neglect of stimulated emission, which tends to make the temperature of A decrease. We have taken the quantized radiation field and an atomic model of the black bodies, and solved for the temperatures of the bodies as a function of time. Density matrix techniques are used. We find that A and B cool down initially, but at different rates, and that as $t \rightarrow \infty$ they approach a common equilibrium temperature.

5.2 Temporal Behavior of Laser Radiation below and above Threshold

Below threshold the problem of the laser statistics may be obtained by conventional mathematics. This is in contrast to the situation above threshold where the general solution may be obtained only by numerical integration. It

is planned to carry out certain calculations in order to provide a detailed check with recently obtained experimental data.

5.3 On the Laws of Planck and Wien¹¹

In a paper with Prof. A. Hill we have discussed the distribution of Planck and Wien in view of recent work on the statistical properties of radiation. One result of these studies shows that while the energy density of the Planck and Wien distributions are almost the same (and in fact identical at high frequencies) higher order correlations are very different at all frequencies.

Publications:

- ¹M. Scully, "Quantum Electronics in Quantum Electrodynamics", McGraw Hill Encyclopedia of Science and Technology 1968 yearbook.
- ²M. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser, I. General Theory", Phys. Rev. 159, 208, 1967.
- ³M. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser, II. Spectral Profile", Phys. Rev. 166, 246, 1968.
- ⁴M. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser, III. Theory of Photoelectron Counting Statistics", to be published.
- ⁵D. Kim, M. Scully and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser, IV. Temperature Effects and Frequency Pulling", submitted to Phys. Rev.
- ⁶D. Kim, M. Scully, and W. E. Lamb, Jr., "Quantum Theory of an Optical Maser. V. Atomic Motion and Recoil", submitted to Phys. Rev.
- ⁷M. Scully, "On Coherence in Quantum Mechanics", Proc. of Inter. Atomic Physics Conf., June 1968. To be published, Gordon and Breach, N.Y.
- ⁸F. Hopf and M. Scully, "Theory of an Inhomogeneously Broadened Amplifying Medium", Phys. Rev., to be published.
- ⁹M. Scully, M. J. Stephen and D. C. Burnham, "Photon Echo in Gaseous Media", Phys. Rev. 171, 213, 1968.
- ¹⁰M. Scully and P. Lee, "Frequency Pulling Effects in Josephson Radiation", submitted to Phys. Rev. Letters.
- ¹¹A. G. Hill and M. Scully, "The Laws of Planck and Wien Revisited", Am. J. Phys., submitted for publication.

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

Dr. C. A. Kocher, National Science Foundation Postdoctoral
Fellow, Physics

Graduate Students:

G. N. Carter, Research Assistant, Physics

F. Y. Chu, 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:

D. E. Pritchard, Ph.D. (Harvard University), February, 1968

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 Aeronautics and Space Agency, NGR 22-009-247, DSR 70955

Advanced Research Projects Agency, SD-90, DSR 75107

1.0 Low Energy Photon Counter

Personnel: Professor D. Kleppner; Dr. M. Than Myint

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, in which case the device might operate as an infrared photon counter. This could provide an increase in sensitivity of many orders of magnitude over present infrared detectors. Applications for such a device would be numerous.

Our initial studies have involved detecting the energy loss of alpha rays which penetrate the superconducting thin film. The behavior of the detector is in reasonable agreement with our predictions for the threshold conditions for particle detection. In order to detect low energy particles we will have to use films with higher current densities (the sensitivity varies as the fourth power of current density), and we are currently exploring techniques for achieving this. Since present films operate at much lower densities than have been achieved elsewhere, we are optimistic about improvements.

We have used alpha particles to trigger the detector because of the ease of with which they can be produced. However, in order to investigate accurately the sensitivity of the detector to particle energy and to the operating parameters, we must provide a controlled energy source. Towards this end, we are currently designing a new cryostat which will permit injection of electrons or photons.

2.0 Magnetic Moment of the Proton

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

Research Report

This is a continuing effort to yield a more precise value of the proton magnetic moment in terms of the Bohr magneton: The experiment utilizes a hydrogen maser which operates in a magnetic field of 3,500 G. The electron and proton are simultaneously flipped by a double resonance technique.

We have improved the magnetic field homogeneity to the point where the electron radiation lifetime is as long as 4 millisecs, corresponding to a linewidth of 80 Hz at a frequency of 9.2 GHz. Because fluctuations in the field of as little as 1 part in 10^8 cause appreciable

broadening of the resonance line, we have introduced a procedure of using a boxcar integrator to observe free precession of the electron line. In this manner the "instantaneous" double resonance curve can be obtained in contrast to the previous method of observing the effect of the proton resonance on the average value of the electron line.

Under favorable conditions, the statistical spread of the observed proton moment is several parts in 10^8 , so that a final determination to one part in 10^8 seems quite feasible. However, there are a number of sources of non-statistical error which may effect the results, and these are currently under study.

3.0 Spin-Exchange Scattering

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

Our new technique for observing spin-exchange scattering between atoms has been successfully applied to a variety of alkali-alkali systems during the past year. Briefly, the method involves measuring the differential cross section for scattering of thermal atoms in which the initial and final spin state of the scattered atom is known. The apparatus involves crossed atomic beams. A velocity analyzer is used to give good momentum resolution. Because the spin-state is known, we can separately measure the singlet and triplet potentials. (The triplet state is dominantly repulsive and has no bound states - consequently it cannot be determined from spectroscopic measurements.)

We have measured spin-exchange cross sections in the following systems: Na-Cs, Na-Rb, Na-K, K-Cs, K-Rb. In each case we have been able to determine the depth of the triplet potential well formed at large distances where the Van der Waals attraction dominates the exchange repulsion. The well depth is of the order of 10^{-2} eV, at an interatomic distance of typically, $12 a_0$. We are currently in the process of making a detailed comparison between the data and existing theoretical predictions for the exchange potentials.

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. Maglic, Research Assistant, Physics

A. C. Nunes, Research Assistant, Physics

C. Stassis, Research Assistant, Physics

Personnel who have left:

C. S. Schneider (Now Department of Science, U. S. Naval Academy,
Annapolis, Maryland)

Sponsorship:

U. S. Atomic Energy Commission, Contract AT(30-1)-3031,
DSR 79210, 71104

National Science Foundation, Grant GP-6195, DSR 70038, expired 3/14/68
Grant GP-8303, DSR 70981

Research Report

1.0 Ferromagnetic Prism Refraction of Neutrons

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

Sponsorship: National Science Foundation

The very high angular resolution of a double crystal spectrometer using a matched pair of perfect silicon crystals has been exploited in studying prism refraction effects with neutrons. Most effort has been concentrated on studies with ferromagnetic prisms where a spin splitting of an unpolarized incident beam is found, completely analogous to the historic Stern-Gerlach experiment. This has been exploited to yield an

accurate determination of the forward magnetic scattering amplitude for pure iron which agrees with that calculated from bulk magnetization to better than one percent. Thus the 10 percent discrepancy between the expected forward amplitude (calculated from magnetization) and that extrapolated from the experimental Bragg amplitudes (3d-like) is confirmed and this substantiates further the presence of a non-3d-like negative magnetization component. The refractive bending angles are very small (1 to 15 seconds of arc) and an accurate calibration of the angular sensitivity of the spectrometer system has been carried out with optical fringe measurements. Studies have also been performed on cascaded prism assemblies wherein double Stern-Gerlach splitting is investigated. Rotation of the neutron polarization by resonance means between separated Stern-Gerlach components has demonstrated the basic quantum-mechanical resolution of spin $1/2$ states.

2.0 Refractive Bending of a Neutron Beam by a Magnetic Field

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

Sponsorship: National Science Foundation

Studies similar to (A) have been performed with pure magnetic fields shaped with prism and cylindrical geometry. The deflection and focussing effects are being remeasured making use of improved angular calibration data and the experimental results are being compared with those calculated from the field contour distribution determined by Bi-probe scanning.

3.0 High Temperature Study of Iron Magnetic Scattering Amplitudes

Personnel: R. Maglic

Sponsorship: National Science Foundation

The magnetic contribution to the Bragg structure factor for iron is being studied at high temperature (up to the Curie temperature) for comparison with the magnetization and for assessment of the temperature variation of spatial asymmetry of the magnetic 3d electrons. The high temperature vacuum furnace, mounted in a vertical field electromagnet on the polarized beam spectrometer, has been improved and a careful

assessment of the crystal extinction, higher-order wavelength, beam depolarization and zero-field extrapolation effects has been made during the past period.

4.0 Single Slit Diffraction of Neutrons

Personnel: Professor C. G. Shull

Sponsorship: U. S. Atomic Energy Commission at Brookhaven National Laboratory and National Science Foundation

The diffraction broadening of a neutron beam in passing through a fine slit has been studied by laboratory personnel using a high angular resolution spectrometer set up at Brookhaven National Laboratory. Long wavelength neutrons ($4.4\text{\AA}$) were used on a double crystal spectrometer (perfect silicon crystals in parallel orientation) and these were passed through slit openings ranging between 4 and 21 microns fabricated with metallic Gd edges for high edge absorption. The observed broadening (4 to 20 seconds of arc) agreed well with that calculated for Fraunhofer diffraction and demonstrated that the neutron wave front was coherent over a transverse length at least that of the largest slit opening used in the experiment.

5.0 Studies of (222) Forbidden Germanium Reflection

Personnel: A. C. Nunes

Sponsorship: U. S. Atomic Energy Commission

A study of the (222) Bragg reflection in germanium is being carried out with neutrons at room temperature and at elevated temperatures. 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. Present neutron observations, carried out elsewhere and here, have shown no measureable neutron reflectivity at room

temperature. Hence the bulk of the x-ray intensity effect must arise from model (1) above. There is good reason to believe however that model (2) should also be a contributing factor and present efforts are directed toward repeating the neutron experiment at high temperature (400-500°C) where effects arising from model (2) will be considerably enhanced. Aside from the room temperature measurements and the preparation of a furnace for the high temperature measurements, theoretical analysis has been given to the high temperature case which will guide the eventual interpretation of the experiment.

6.0 Studies of Coherent Paramagnetic Scattering by Vanadium

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

Sponsorship: U. S. Atomic Energy Commission

The weak paramagnetism in vanadium metal can be studied by polarized neutron scattering in coherent Bragg reflections when a magnetic field is applied to the crystal. We have been interested in seeing whether this coherent paramagnetic scattering is modified below the superconducting transition (T_c about 5°K) thereby indicating an electron-spin pairing action as previously studied in superconducting V_3Si . Several specimen crystals of varying purity (residual resistance ratios varying between 20 and 120) were studied during the period with essentially identical results. The observations, when corrected for nuclear polarization effects at low temperature, suggest a modification of the paramagnetic scattering below T_c in spite of the presence on the crystal of a magnetic field of 14,000 gauss much higher than the critical field for vanadium. This observation would imply that electron-spin pairing is still effective below T_c even though the bulk, transport superconductivity effects have been suppressed by the applied field. It is recognized that the residual effects and their interpretation are sensitive to the nuclear polarization correction that must be applied to the data and that an error in applying this correction can remove the effect. Further work in confirming the degree of nuclear polarization is called for before the conclusion can be accepted.

7.0 Study of Kondo Effect in Dilute Alloys

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

Sponsorship: U. S. Atomic Energy Commission

When magnetic impurity atoms are introduced into a non-magnetic host lattice in dilute form, there has arisen in the last few years considerable theoretical evidence, supported by some experiments, that an anti-ferromagnetic bound state exists between the impurity magnetic atom and the surrounding conduction electrons of the metal lattice. It may be possible to observe this coupling directly by polarized neutron scattering at low temperatures (below the Kondo temperature) and a start has been made at preparing suitable crystal specimens for study. The system Cu-Fe with 0.1 percent Fe composition has been selected for study. Crystals of the alloy have been grown and homogenized and exploratory neutron studies are about to begin.

8.0 Neutron Diffraction by Perfect Crystals

Personnel: Professor C. G. Shull (on leave at Brookhaven National Laboratory); Drs. R. Nathans and H. Alperin (Brookhaven National Laboratory)

Sponsorship: U. S. Atomic Energy Commission

Experiments have been started which are designed to test implications of dynamical theory (in which the intimate relationship between Bragg reflected and forward reflected radiation within the perfect crystal volume is emphasized) for the neutron case. Experiments with perfect silicon crystals have been performed for which there is very small neutron absorption and this permits novel testing of the theory compared with x-ray observations. Of interest in the experiments is the spatial distribution of Bragg intensity being released by the crystal as a function of incident ray direction. Two general conclusions have become available from the study: (1) Bragg reflected intensity always arises from crystal surface source points and not volume points and (2) all Bragg reflected beams contain within themselves an intimate Pendellosung interference fringe structure. The latter fringe structure is very sensitive to experimental parameters such as the neutron wavelength and nuclear scattering amplitude and has been used to determine the nuclear scattering amplitude for silicon with a precision much higher than previously available. In this way, the atomic scattering amplitude for silicon has been determined as $0.41646 \pm 0.00022 \cdot 10^{-12}$ cm. With this precision, the neutron-electron

interaction amplitude of $-0.00140 \cdot 10^{-12}$ cm must be allowed for in arriving at the true nuclear scattering amplitude. The interference fringe effects that have been measured also yield novel information on the longitudinal extent of the coherently-split neutron wave packet as it travels through the crystal.

Theses:

- C. S. Schneider, "The Forward Magnetic Scattering Amplitude of Iron for Thermal Neutrons by Prism Refraction", Ph. D., Department of Physics, September, 1968.

Publications:

- C. G. Shull, "Neutron Interactions with Atoms", Trans. Amer. Crystal. Assoc. 3, p. 1 (1967).
C. G. Shull, "Spin Density Distribution in Fe, Co, and Ni", Symposium on Magnetic and Inelastic Scattering of Neutrons by Metals, Gordon and Breach Science Publishers, Inc., New York, 1967.
C. G. Shull and R. A. Nathans, "Search for a Neutron Electric Dipole Moment by a Scattering Experiment", Phys. Rev. Letters 19, 384 (1967).
C. G. Shull, K. R. Morash and J. G. Rogers, "Specimen Motion Effects in Neutron Diffraction", Acta Cryst. A24, 160 (1968).

V. THE SPECTROSCOPY OF LIGHT SCATTERED FROM THERMAL
FLUCTUATIONS IN LIQUIDS; SOLIDS, AND GASES

Faculty:

G. B. Benedek, Professor, Physics

Research Staff:

J. B. Lastovka, DSR Staff, Center for Materials Science and
Engineering

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

D. Schaefer, National Science Foundation Post Doctoral Fellow

D. Hammer, Visiting Scientist, Physics

Graduate Students:

D. Cannell, Research Assistant, Physics

N. Clark, Research Assistant, Physics

S. B. Dubin, Research Assistant, Physics

J. Lunacek, Research Assistant, Physics

P. Lazay, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and
Engineering

Personnel who have left:

D. Hammer

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75102

Sloan Fund for Basic Research in the Physical Sciences (Sloan Fund
27731)

U.S. Army Research Office-Durham, DA-31-124-ARO-D-425, DSR 76210

National Aeronautics and Space Administration NGR-22-009-182,
DSR 76375

National Aeronautics and Space Administration NGR-22-009-249,
DSR 70915

1.0 The Spectrum of Light Scattered From SF₆ Near Its Critical Point

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

Object:

To determine the temperature and density dependence of the thermal diffusivity ($\lambda/\rho C_p$) in the vicinity of the critical point in SF₆.

Research Report

Equipment has been designed, constructed and assembled which will permit simultaneous measurements of the equation of state and the line width of laser light quasi-elastically scattered from SF₆ near its critical point. The latter measurement provides the ratio of thermal conductivity λ and the specific heat. With this new experiment it will be possible to establish conclusively the nature of the divergence of the thermal conductivity of the apparently anomalous fluid near the critical point.

2.0 The Intensity and the Spectrum of Light Scattered Quasi-elastically From Xenon Near Its Critical Point

Personnel: G. B. Benedek; M. Giglio

Object:

To determine the detailed nature of the divergences of the wavelength dependent compressibility and the thermal conductivity near the critical point xenon.

Research Report

Despite the passage of fifty years since Ornstein and Zernike produced their famous paper on the angular disymmetry and the divergence in the intensity of light scattered from a fluid near its critical point, no reliable data exists in the literature which substantiates this theory for a single component fluid or uses it to measure the divergence of the compressibility near the critical point. Dr. Giglio has constructed a unique light scattering cell which is capable of simultaneous, precise measurements of the intensity and the line width of the scattered light scattered

from xenon near its critical point along a whole series of paths around and through the critical point. The equipment is now about completely assembled and its operation should provide the most complete information yet produced on the dynamical and equilibrium properties of a simple fluid near its critical point.

3.0 The Brillouin Spectrum of Light Scattered From Xenon Near Its Critical Point

Personnel: G. B. Benedek; D. Cannell

Object:

To determine the temperature dependence of the transport coefficients which are responsible for the sound attenuation near the critical point of xenon.

Research Report

After the operation of our initial system for the study of the Brillouin spectrum a double, spherical scanning Fabry-Perot spectrometer with extremely high skirt selectivity has been constructed and put into operation. Our early results on CO_2 were presented at the Boston Meeting of the American Physical Society, Bull. Am. Phys. Soc. II 13, 183 (1968). The newly completed experimental apparatus is now beginning to provide very accurate results on the Brillouin spectrum in xenon.

4.0 The Spectrum of Light Quasi-elastically Scattered From Solutions of Biological Macromolecules

Personnel: G. B. Benedek; S. B. Dubin, D. Schaefer, P. Cvitanovic

Object:

To measure the diffusion constants of biological macromolecules from the spectrum of scattered laser light as a means of determining (a) changes in molecular conformation (b) molecular weights (c) the microscopic hydrodynamic behavior of viruses.

Research Report

Dr. D. Schaefer is studying the angular variation of the spectral shapes of light scattered from tobacco mosaic virus: This experiment will provide a means of determining whether departures from Lorentzian line shapes can be used to determine both rotational diffusion constants and anisotropic translational diffusion constants for this rod shaped virus. This in turn should provide an important test of the usefulness of the light scattering spectra as a means of obtaining detailed information on the hydrodynamics of these viruses. Mr. P. Cvitanovic is undertaking the measurement of the diffusion constant and molecular weight of the "30S" and "50S" constituents of bacterial ribosomes. These ribosomes constitute the factory where protein synthesis takes place, and establishment of the molecular weight of the ribosomal constituents is of great importance to molecular biology. Mr. Dubin, in conjunction with Professor D. Friefelder of Brandeis and Dr. C. Bancroft of Harvard has measured with very high precision the diffusion constants of several bacteriophages mainly T_7 , T_5 , T_4 and λ . By combining these results with measures of the sedimentation velocity and partial molal volume we are able to measure for the first time the molecular weights of these phages.

Finally, we are conducting with Professor G. Feher of the University of California LaJolla, a study of the conformational changes that occur on the denaturation of lysozyme under the action of guanidine hydrochloride. We have been able to establish clearly that the molecular diffusion constant decreases by 30% under the action of 5 molar guanidine. Detailed measurements in the transition region around 3 molar guanidine are in progress to establish the precise form of the dependence of D on guanidine concentration.

5.0 The Spectrum of Light Scattered From Density Fluctuations in Gases

Personnel: G. Benedek and T. Greytak; N. Clark

Object:

To study the time dependence of the density fluctuations both in single component gases and in gas mixtures.

Research Report

Mr. Clark has constructed a 20 milliwatt single-frequency stabilized helium-neon laser with a frequency stability of $\sim \pm 750$ kHz. He has also constructed a scattering cell for gases in which the pressure can be varied from 10 mm Hg to 10 atmospheres, and flat and spherical Fabry-Perot interferometers for the spectral analysis of the scattered light. He now has obtained the spectra of light scattered from pure xenon at pressures of 10 mm Hg, 20 mm, 40, 50 and 100 mm Hg. Also he has the spectra of light scattered from xenon-helium mixtures in which the xenon partial pressure is 10 mm and the helium partial pressure is ~ 100 mm, 300 mm, 500 mm and 750 mm Hg. This data will permit a detailed check of the theory of Professor S. Yip on the transition in the spectral shape between free flights regime and the random walk regime in the movement of the xenon atoms. The former regime applies when the mean free path is large compared with the wavelength of the scattering fluctuations. The latter regime applies when the mean free path of the xenon molecules is small compared to the fluctuation wavelength.

6.0 The Velocity and Attenuation of Hypersonic Sound Waves in Ammonium Chloride

Personnel: G. B. Benedek; P. Lazay, J. H. Lunacek

Object:

To determine the velocity and the attenuation of microwave frequency sound waves in NH_4Cl as a function of temperature.

Research Report

Mr. Paul Lazay has completed a study of the Brillouin spectrum of light scattered at 90° from NH_4Cl from room temperature to below the critical point at -30°C . Using the high resolution grating spectrograph at the MIT Spectroscopy laboratory. His measurements show that there is a marked dispersion in the sound velocity for sound waves of ~ 18 GHz, and that this dispersion is temperature dependent. He also observed a natural width of the Brillouin component in this solid. This observation was confirmed by Mr. N. C. Clark and Mr. J. Lunacek, who measured the frequency dependence of the line width in NH_4Cl at room temperature using Fabry-Perot plates and a high power single mode laser. This work, along with simultaneous measurements by A. Pine and G. Durand at

Harvard on quartz, represent the first observation of the natural line widths of the Brillouin components in solids. These observations open the door to detailed study of the mechanism of high frequency sound attenuation in solids. Mr. Lazay is now writing his Ph.D. thesis. Mr. Lunacek is extending the line width measurements down to lower temperatures in order to detect the increased attenuation that should occur near the order-disorder phase transition at -30°C . Finally it should be pointed out that there is a striking increase in the intensity of light scattering near the order-disorder transition in NH_4Cl . There is considerable question as to whether or not this increase in intensity is associated with a divergence in the specific heat of the solid at that point. In order to settle this matter Professor Benedek has proposed an experiment to give the spectral analysis of the quasi-elastic scattering near this point. From the temperature dependence of this spectral width one can decide whether the divergence in the intensity is indeed associated with a true critical slowing down of the entropy fluctuations. This proposal will appear in the Proceedings of the International Conference on Light Scattering, N. Y., September 3-6, 1968, New York University.

Publications:

- G. B. Benedek and D. S. Cannell, "Brillouin Scattering in Carbon Dioxide Near Its Critical Point," *Bull. Am. Phys. Soc. II*, 13, 182 (1968).
- J. H. Lunacek, N. Clark, P. Lazay and G. Benedek, "Observation of the Natural Linewidth of the Brillouin Components of Light Scattered by a Solid," *Bull. Am. Phys. Soc. II*, 13, 183 (1968).
- P. Lazay and G. B. Benedek, "Rayleigh-Brillouin Spectrum of NH_4Cl ," *Bull. Am. Phys. Soc. II*, 13, 183 (1968).
- G. B. Benedek, "Spectrum of Light Scattered by Critical Fluctuations," *Proc. International Conference on Light Scattering*, Ed. A. McWhorter and G. Wright, J. Springer and Co. (in press).
- P. D. Lazay, J. H. Lunacek, N. A. Clark and G. B. Benedek, "The Rayleigh-Brillouin Spectrum of Ammonium Chloride," *Proc. International Conference on Light Scattering*, J. A. Springer and Co., Ed. A. McWhorter and G. Wright.
- G. B. Benedek, "Optical Mixing Spectroscopy; With Applications to Problems in Physics, Chemistry, Biology and Engineering," to be published in the A. Kastler Jubilee Volume, Paris, 1968.

VI. OPTICAL SPECTROSCOPY OF MAGNETIC SOLIDS NEAR THE
CRITICAL POINT

Faculty:

J. D. Litster, Assistant Professor, Physics

Graduate Students:

J. Ho, Research Assistant, Physics

T. Stinson, National Science Foundation Fellow, Physics

D. D. Berkner, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and
Engineering

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75101

National Aeronautics and Space Administration NGR-22-009-182,
DSR 76375 (from February 1, 1968)

1.0 Faraday Rotation in Magnetic Systems Near the Critical Point

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

Object:

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

Research Report:

1.1 Faraday Rotation in CrBr_3

We have assembled a temperature controlled optical dewar system capable of maintaining our sample within less than one mdeg K of any desired temperature from 4.2°K to 100°K. Our optical system enables us to measure rotations of the plane of polarization as small as 5×10^{-5} radians.

With this system we have used the Faraday effect to measure the magnetization along 21 isotherms from $T_c - 400 \text{ mdeg} < T < T_c + 2200 \text{ mdeg}$ in external fields up to 1000 G. We have been able to measure the magnetization to an accuracy of 1 part in 10^4 of the saturation magnetization at 0°K .

Analysis of these data reveals the divergences of the magnetic properties in the critical region to be as follows: Along the critical isochore the susceptibility diverges as $(T/T_c - 1)^{-\gamma}$ with $\gamma = 1.215 \pm 0.02$. The magnetization along the critical isotherm is proportional to $H^{1/\delta}$ when $\delta = 4.28 \pm 0.1$. The spontaneous saturation magnetization goes to zero as $(1 - T/T_c)^\beta$ with $\beta = 0.368 \pm 0.005$.

We define the scaled magnetization by $m = \sigma |t|^{-\beta}$ and the scaled magnetic field by $h = H |t|^{-\beta\delta}$, where σ is the reduced magnetization, H the internal magnetic field, and $t = (T - T_c)/T_c$. From our data we find the equation of state to have the form

$$h = F(m)$$

and are able to determine the mathematical form of F with greater precision than has been possible for any other critical system.

These preliminary results will be presented at the 1968 Magnetism Conference, and we are continuing our experiments to determine the region over which the scaling law equation of state is valid.

This method is presently being used to study EuS and EuO as well.

1.2 Faraday Rotation in Y.I.G.

An optical system has been assembled that will enable us to measure Faraday rotation in yttrium iron garnet (YIG) at 1.15μ . We have built and put into operation a small oven that will fit between the pole caps of our 12" electromagnet and provide precise temperature control of our sample in the temperature range around 550°K . This system will be used shortly to make measurements on YIG similar to those carried out on CrBr_3 .

2.0 Brillouin Scattering Near the Melting Point of Crystalline Solids

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

Object:

To study the phonon spectrum of crystalline solids near the melting point by means of Brillouin scattering.

Research Report:

We have assembled a Fabry-Perot interferometer for spectral analysis and a photomultiplier tube using electron counting for the detection of the scattered light.

Initial experiments will be conducted on alum using a helium neon laser. A temperature control system to operate in the vicinity of the melting point of alum has been constructed and put into operation.

Publications:

J. D. Litster, "Using the Laser as a Probe of Matter," Tech. Engineering News, Vol. XLVIII, (December 1967).

J. T. Ho and J. D. Litster, "Divergences of the Magnetic Properties of CrBr_3 Near the Critical Point," J. Appl. Phys. (to be published).

VII. LIGHT SCATTERING FROM EXCITATIONS IN HELIUM⁴ AND HELIUM³-HELIUM⁴ MIXTURES

Faculty:

T. J. Greytak, Assistant Professor, Physics

Graduate Students:

R. St. Peters, N.S.F. Predoctoral Fellow, Physics

J. Yan, Research Assistant, Physics

R. Benjamin, Research Assistant, Physics

Support Staff:

Malinda Rieck, Secretary, Center for Materials Science and
Engineering

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75103

1.0 Brillouin Scattering in the Superfluid Phase of He⁴

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

Object:

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

Research Report:

We have measured the velocity of 700MHz phonons with a precision of 1% from 1.6°K to the lambda point, $T_\lambda = 2.17^\circ\text{K}$, and we have been able to observe lifetimes qualitatively in a portion of this temperature region. In order to achieve a higher precision in the velocities, and to make possible quantitative measurements of lifetimes, we have developed an ultra-high resolution spherical Fabry-Perot interferometer whose line width of 4MHz corresponds to a resolution of better than 10^8 . Our instrumental width is now equal to or less than the spectral widths we wish to measure. We have added a fast pump to the dewar system to

achieve temperatures as low as 1°K . To facilitate experiments very close to the lambda point we have built a temperature stabilizing servo system. As soon as the single mode laser discussed below is completed, it will be shared with this experiment and we will begin taking higher resolution spectra.

2.0 Scattering from Thermal Fluctuations in He^3 - He^4 Mixtures

Personnel: T. J. Greytak; R. Benjamin

Object:

To study the velocities and lifetimes of first and second sound and the relaxation time of concentration fluctuations in the superfluid phase of He^3 - He^4 mixtures. The distribution of energy among these fluctuations in thermal equilibrium can also be obtained.

Research Report:

We have modified a commercial He-Ne laser to operate in a single mode, and we are adding a servo system to stabilize its absolute frequency. This will provide the stable, powerful, single frequency source required in this experiment due to the weak scattering cross-section and small frequency shifts that are predicted.

3.0 Raman Scattering from Rotons in He^4

Personnel: T. J. Greytak; J. Yan

Object:

To measure the energies and lifetimes of excitations near the minimum (rotons) and the maximum of the dispersion curve in liquid helium.

Research Report:

A Raman scattering system has been assembled consisting of a powerful He-Ne laser, grating spectrograph, and photon counting detection. It is capable of detecting excitations in helium whose cross-section is as

small as 10^{-3} of that due to the phonons at 2°K (which we are already studying in our other experiments). We have designed and assembled a special He dewar system for this experiment, which we are in the process of testing. When it is working satisfactorily, we will begin searching for this effect.

Publications:

T. J. Greytak, R. L. St. Peters, and G. B. Benedek, "Brillouin Scattering in Liquid Helium", Bull. Am. Phys. Soc. 13, 183 (1968).

VIII. 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, NSF Trainee, Chemistry
R. T. Ruettinger, Research Assistant, Chemistry
N. E. Schumaker, Research Assistant, Chemistry
D. D. Snyder, Research Assistant, Chemistry
B. B. Weiner, NSF Trainee, Chemistry
R. A. Young, Research Assistant, Chemistry

Personnel who have left:

R. T. Ruettinger; to Department of Biology, MIT
N. E. Schumaker; to Bell Telephone Laboratories, Murray Hill, N.J.
D. D. Snyder; to A. D. Little, Cambridge, Mass.
R. A. Young; to IBM Corporation, Chicago, Illinois

Degrees Granted:

R. T. Ruettinger, S.M., Chemistry, September 1968
N. E. Schumaker, Ph.D., Chemistry, June 1968
D. D. Snyder, Ph.D., Chemistry, September 1968
R. A. Young, Ph.D., Chemistry, June 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75104
National Science Foundation Grant, GP-7738, DSR 70706 (terminated
9/15/67) GP-5042, DSR 76047 (commenced 9/16/68)
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. Garland; E. Litov; D. Eden, P. Mueller, D. Snyder,
R. Young

1.1 Phase Transitions in Ammonium Bromide

The adiabatic elastic constants of single-crystal ammonium bromide have been measured at 20MHz as functions of temperature and pressure in the region from 180 to 240°K and from 0 to 6 kbar. A new high-pressure ordered phase, denoted as 0_{II} , has been discovered in this temperature range. The acoustic properties of this new 0_{II} phase were investigated with emphasis on the regions of the first-order phase transition from the 0_{II} phase to the ordered tetragonal phase and the lambda transition from the 0_{II} phase to the disordered cubic phase. The region of the lambda transition from the ordered tetragonal phase to the disordered cubic phase was also studied. This work is now complete, and a detailed manuscript describing our results should appear in the December 15, 1968 issue of the Journal of Chemical Physics.

1.2 Velocity and Attenuation in KH_2PO_4

The ultrasonic data obtained by Dr. D. B. Novotny (during 1966-67) have been subjected to a careful review and a new analysis has been made of his data in the paraelectric phase. The abstract of a manuscript (to be published in the Physical Review) describing these results reads "The velocity and attenuation of ultrasonic shear waves have been investigated at temperatures above $T_c = 121.8_2^0$ K in single-crystal KDP. An elastic Curie-Weiss law, $(s_{66}^E - s_{66}^P) = D/(T - T_c)$, is obtained with an elastic Curie constant D equal to $6.31 \times 10^{-11} \text{ dyn}^{-1} \text{ cm}^2 \text{ deg}$. The attenuation data are consistent with a cooperative relaxation time at constant stress τ which varies as $\tau = 24 \times 10^{-12} / (T - T_c) \text{ sec}$ ".

A new cell for the investigation of KDP below T_c (including improved provisions for poling the crystal with an electric field) has been designed and is under construction. Dr. E. Litov has recently joined the group, and he will soon being measurements on the ferroelectric phase of KDP

1.3 α - β Transition in Quartz

The velocities of 30 and 45MHz longitudinal waves propagating in quartz parallel to the X- and Z-axes have been measured as a function of temperature from 500 to 600°C. Only longitudinal waves could be studied because no suitable solid bond was found to transmit shear waves; molten AgCl was discovered to work well in transmitting longitudinal waves. The elastic constants c_{11} and c_{33} were calculated as functions of temperature at 1 atm, and their variations were studied with special care in the immediate region of $T_\lambda = 574^\circ\text{C}$. No unambiguous discontinuity (indicating a first-order instability) could be established from our data, although the recent Brillouin data of Shapiro and Cummins does indicate such an effect. It would appear that very precise temperature stability and resolution is required.

Attenuation of 20 and 60MHz longitudinal waves propagating parallel to the X-axis was also measured. These attenuation data are difficult to interpret but seem to suggest intense acoustic scattering due to domains (microtwinning) over a range of about two degrees near T_λ . Outside this region there is a much lower attenuation which is roughly proportional to the frequency and does not conform to the expected critical variation in the relaxation time.

1.4 Attenuation in NH_4Cl at High Pressures

The attenuation of a longitudinal wave propagating in the [100] direction of NH_4Cl has been measured as a function of temperature and pressure in the vicinity of the lambda line. At seven temperatures between 241.0°K and 270.2°K measurements were made as the pressure was varied from 1 to 3500 bar. Measurements were carried out at 10, 20 and 30MHz using argon gas as the pressure fluid. One-atmosphere attenuation results were reinterpreted using recently obtained high-frequency velocity values from Brillouin scattering (~17 GHz) to calculate the relaxation strength. The relaxation time τ_{SV} was also calculated along isochores V_{242} (34.750 cm³) and V_{273} (34.266 cm³). In the disordered phase, τ_{SV} behaves approximately as $A/(T-T_\lambda)$ along both the V_{242} isochore and the one-atmosphere isobar. In the ordered phase, the τ_{SV} behavior, both at one atmosphere and along V_{273} , is more complicated and does not conform to simple theoretical models. Lines of constant attenuation in the ordered phase lie parallel to the lambda-line; however, lines of constant attenuation in the disordered phase converge rather strongly toward the

lambda line at high pressures. Thus, it appears that the dynamical properties follow a law of corresponding states in the ordered phase but not in the disordered phase (at least for pressures below 3.5 kbar).

An intensifier for our gas-pressure system has recently been obtained and installed. This will make it possible to generate gas pressures up to ~ 10 kbar once some high-pressure leak problems are solved, and it is hoped to extend this NH_4Cl attenuation work above 3.5 kbar.

1.5 Liquid-vapor Critical Point in Xenon

Much progress has been made in the past year, although recurrent experimental problems have prevented the collection of ultrasonic data until recently. Preliminary data on xenon indicates that the "sing-around" method of velocity measurement will not work well without drastic modification. Unfavorable signal-to-noise ratios exist near the critical point due to poor acoustical coupling and high attenuation, and the relatively undamped quartz crystal "rings" for a length of time much longer than the length of the RF pulse applied to it. Therefore, the velocity measurements are being made by observing relative changes in the time delay of an arbitrarily selected cycle in the amplified RF signal from the receiving crystal as the transmitting crystal is moved by known amounts. The peak-to-peak amplitudes measured at the same time and on the same cycle are used to calculate the attenuation. Uncertainties in the delay measurements are about $\pm 0.01 \mu\text{sec}$ and those in the relative spacing of the transducers are about $\pm 0.002 \text{ mm}$. The resulting uncertainties in the velocity are no greater than $\pm 0.7\%$ even near the critical point.

The temperature control of the bath has been improved somewhat, and the temperature can now be held within 0.001°C of a given temperature for at least 24 hours with root-mean-square variations $(10 \text{ sec averaging})$ over a two-hour period being on the order of 0.0003°C . The pressure near the critical point is constant to within the resolution of the pressure measuring equipment (0.003 atm) over this same period of time.

Measurements at 16.94°C (about 0.35°C above the critical temperature) over a narrow range of pressures (58.6 to 57.7 atm) have yielded values of the velocity ranging from 99 m sec^{-1} to 122 m sec^{-1} and values of the attenuation ranging from 255 db cm^{-1} to 5 db cm^{-1} . On the basis of these measurements, it is expected that velocity and attenuation measurements can be made in regions where the attenuation is as large as 500 db cm^{-1} , although with reduced accuracy.

2.0 Infrared Spectroscopy

Personnel: C. Garland; R. Ruettinger, N. Schumaker

2.1 Low-Temperature Spectra of Ammonium Halides

Infrared spectra of sublimed films, single-crystal sections, and pressed disks of NH_4Cl , ND_4Cl , NH_4Br , and ND_4Br have been studied at numerous temperatures between 300°K and 21°K . Spectra recorded at 21°K possess numerous sharp and intense bands. These bands can be assigned to infrared-active fundamentals and multiple combinations involving internal modes of the ammonium ion, librational modes of the ammonium ion, and the intrinsic vibrations of the crystalline lattice. New combination bands involving ν_4 and the lattice modes ν_{TO} and ν_{LO} were observed.

The first overtone of the libration mode ($2\nu_2$) of the ammonium ion has been observed using thin films in all the compounds in their ordered phases. The second overtone ($3\nu_6$) was also observed in spectra from single-crystal sections and pressed disks. The frequencies observed for ν_6 , $2\nu_6$ and $3\nu_6$ are discussed in relation to the model potential described by Gutowsky, Pake, and Bersohn. The barrier height (V_0) for the hindered rotation of the ammonium ion is calculated to be 1860 cm^{-1} ($5.32\text{ kcal mole}^{-1}$) for NH_4Cl and ND_4Cl and to be 1520 cm^{-1} ($4.35\text{ kcal mole}^{-1}$) for NH_4Br and ND_4Br . However, the potential model of Gutowsky, Pake and Bersohn is not sufficiently anharmonic to reproduce accurately the observed frequencies.

The intensity variation of the ν_4 -bending vibration of the ammonium ion was studied in detail. The variation of the intensity of an anomalous high frequency component is correlated with the breakdown of translational symmetry due to the order-disorder transition in NH_4Cl . The phase transitions of NH_4Br are also examined. The ordered cubic phase of NH_4Br is observed to become appreciably disordered before transforming at 108°K into the ordered tetragonal phase, which gives a new insight into the nucleation mechanism of this order-order phase transition.

2.2 Spectra of Mixed Crystals

The infrared spectra of mixed crystals of ammonium chloride and ammonium bromide have been recorded over a wide range of compositions.

Pressed disks of these binary salts were investigated at temperatures between 300 and 21°K. The resulting spectra were compared with the spectra of pure ammonium chloride and pure ammonium bromide, and observations of the effects of halide ion disordering on combination bands of internal and lattice modes have been noted. New components of the overtone of the ammonium ion libration have been observed in mixed crystals, and a correlation of these components with various hydrogen bonding possibilities can be made. The presence of features similar to those observed in the infrared spectra of pure tetragonal ammonium bromide has been noted in the spectra of mixed crystals with high bromide content. This work also provides new information concerning the phase diagram of mixed crystals of ammonium chloride and ammonium bromide.

3.0 Low-Temperature X-Ray Diffraction

Personnel: A. Bonilla, B. Schumaker, R. Young

In connection with some low-temperature infrared spectroscopy on ammonium halide films, it was discovered that the first-order phase transition between cubic parallel-ordered NH_4Br and tetragonal ordered NH_4Br at 108°K was quite complex. The spectra suggested that this order-order transition was "nucleated" by changes occurring in the cubic ordered phases at temperatures far below the transition point. Since X-ray measurements had never been made below ~120°K, we have set up a Cryotip regulator with special shroud to do X-ray work on NH_4Br as a function of temperature down to 21°K. (A measurement at 4.2°K has also been made using a helium dewar.) Preliminary results definitely suggest that there are anomalous features in the thermal expansion of the cubic ordered phase over the range 50 - 100°K. It is hoped to complete this brief investigation within the next month or two.

4.0 Pressure-Volume Measurements

Personnel: C. Garland; B. Weiner

By making direct measurements of the change in volume with pressure on a single crystal of NH_4Cl at several constant temperatures, it is anticipated that we can confirm the existence of a first-order transition which has been strongly suggested by elastic constant measurement near the lambda line. Such a first-order instability associated with the

NH_4Cl lambda transition has been predicted on the basis of a compressible Ising model, but a direct observation of the phenomenon and an investigation of the way in which ΔV changes along the lambda line is important.

A great deal of operating experience has been obtained with the two-stage, double-acting gas compressor capable of generating pressures up to 3.4 kbar. It has been found that for precise pressure control the pressure vessel must be honed in order for the Bridgeman seals to hold gas with minimal leaking. At present, the pressure system leaks at a maximum rate of 0.5 bar per hour at 3 kbar and much lower rates at pressures below 2 kbar. (The pressure is measured using a Manganin coil whose pressure-resistance characteristics have been carefully calibrated against a dead-weight gauge.)

NH_4Cl single crystals have been grown and then fly-cut to a length of about 1 cm with opposite faces held parallel to within 30 millionths of an inch. The sample cell, which consists of a precision 3-lead, parallel-plate capacitor whose lower plate is supported by the crystal, has been constructed, assembled, and tested. The capacitance is measured using an impedance bridge which is driven at 1 khz. A phase-sensitive "lock-in" amplifier (P. A. R. model 121) has been obtained to detect the bridge null point. The capacitance measuring system has been tested using a 1 pf General Radio standard. Thus, all components seem to be operative and data should be forthcoming in the very near future.

Publications:

- C. W. Garland and N. E. Schumaker, "Effect of Ordering on the Infrared Spectrum of Ammonium Chloride", *J. Phys. Chem. Solids*, **28**, 799 (1967).
- C. W. Garland and R. A. Young, "Order-Disorder Phenomena VI: Anomalous Changes in the Volume of Ammonium Chloride", *J. Chem. Phys.*, **48**, 146 (1968).
- C. W. Garland, Book Review of "Ultrasonic Absorption", by A. B. Bhatia in *Physics Today*, **21**, 101 (1968).
- C. W. Garland and R. A. Young, "Elastic Constants of Ammonium Bromide. II. High-pressure Ultrasonic Investigation of the Phase Transition", *J. Chem. Phys.* (in press).
- C. W. Garland and D. B. Novotny, "Ultrasonic Velocity and Attenuation in KH_2PO_4 ", *Phys. Rev.* (in press).

IX. CRYSTAL AND SURFACE STRUCTURE INVESTIGATIONS of
Metals, Zeolites, and Other Substances by X-ray, Neutron,
and Electron Diffraction

Faculty:

D. P. Shoemaker, Professor, Chemistry

Research Staff:

Dr. Clara B. Shoemaker, Research Associate, Chemistry

Graduate Students:

M. A. Taylor, Research Assistant, Chemistry

J. G. Keil, Research Assistant, Chemistry

P. C. Manor, Research Assistant, Chemistry

Roberta Ogilvie, Research Assistant, Chemistry

Support Staff:

Janet Pollock, Secretary, Chemistry

Personnel who have left:

M. A. Taylor to Department of Chemistry, Illinois State University

J. G. Keil to Motorola Research Laboratories, Phoenix, Arizona

Degrees Granted:

J. G. Keil, Ph.D., Chemistry, June 1968

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

Sponsorship: Army Research Office, Durham

The $\underline{\text{nu}}$ phase $\text{Mn}_{81.5}\text{Si}_{18.5}$ was found to be body-centered orthorhombic with approximate cell dimensions $a = 17.01$, $b = 28.76$, $c = 4.65 \text{ \AA}$, $Z \sim 190$ atoms per unit cell. The intensity pattern is strongly pseudo-hexagonal around the c axis and shows a resemblance to the P phase intensity pattern. A structure model with 186 atoms per unit cell in space group Immm and consisting of four P-phase fragments related by mirror planes fits the diffraction pattern qualitatively. Over 3000 intensity data have been collected on a fully automated diffractometer to test further and refine the structure. The $\underline{\text{K}}$ phase $\text{Mn}_{77}\text{Fe}_4\text{Si}_{19}$ was found to be monoclinic with $a = 13.32$, $b = 11.61$, $c = 8.68 \text{ \AA}$, $\alpha = 90^\circ$, $Z \sim 114$ atoms per unit cell, space group C2, Cm, or C2/m. The structure appears to be related to that of the delta phase; there appear to be sigma-phase-type layers parallel to (110) planes. Intensity data have been collected on a diffractometer and a Patterson function has been calculated. Both the $\underline{\text{nu}}$ and $\underline{\text{K}}$ phase specimens were kindly provided by Professor Paul Beck, University of Illinois.

Continuity attempts to obtain large Co-V sigma-phase single crystals for polarized beam neutron diffraction work have not been successful.

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

Sponsorship: Humble Oil and Refining Company

Work has continued on studies of hydrogen positions in hydrogen-form faujasite by neutron diffraction, and on the structure of a new zeolite, but without definitive results.

3.0 Low-Energy Electron Diffraction (LEED)

Sponsorship: National Science Foundation, Advanced Research Projects Agency

Work on (110) cleavage surfaces of sphalerite-type ZnTe, CdTe, and ZnSe, and on (2 $\bar{1}$ 10) cleavage surfaces of wurzite-type CdSe, has been completed. No surface superstructures were found. Intensity profiles of (00) reflections were interpreted in terms of an asymmetric absorption model. Shifts of the Bragg maxima indicated an effective inner potential of about 17 volts in all cases. The ZnSe studies had to be conducted at a specimen temperature of 550 $^\circ\text{K}$ owing to the large electrical resistivity at

room temperature. The CdSe ($2\bar{1}\bar{1}0$) patterns in normal incidence showed absences of odd $h0$ beams as required by surface symmetry, but these beams appeared with the specimen tilted so that the incident beam was not parallel to the glide plane; the latter result, not predicted by kinematical theory, demonstrates dramatically the shortcomings of that theory for LEED. Sticking probabilities for O_2 , CO, and H_2 on the cleavage surfaces was found to be less than 10^{-8} .

Vacuum-cleaved zinc (0001) surfaces gave good diffraction patterns with the expected mesh at 100°K failing to show any superstructure. Patterns tended to be washed out by thermal motion at room temperature, particularly above 200 volts. Attempts to produce ordered physically absorbed layers of Xe, O_2 , CO, and benzene at temperatures as low as 100°K produced only amorphous layers and gradual reversible obscuration of the hexagonal (0001) pattern. No evidence of chemisorption was obtained.

Theses:

- J. G. Keil, "LEED Surface Studies of II-VI Semiconductor Compounds,"
Ph.D. Thesis, June 1968.

Publications:

- D. P. Shoemaker and C. B. Shoemaker, "Sigma-Phase-Related Transition Metal Surfaces with Tetrahedral Interstices," Chapter in "Structural Chemistry and Molecular Biology: A Volume Dedicated to Linus Pauling by his Students, Colleagues, and Friends", San Francisco, W. H. Freeman, p. 718 (1968).
- D. P. Shoemaker, "Optimization of Counting Times in Computer-Controlled X-ray and Neutron Single-Crystal Diffractometry", *Acta Cryst.*, A24, 136 (1968).
- L. G. Feinstein and D. P. Shoemaker, "Polarized Neutron Diffraction Study of Ordered VFe", *J. Phys. Chem. Solids*, 29, 184 (1968).
- C. B. Shoemaker and D. P. Shoemaker, "Structural Properties of some σ -Phase Related Phases". Chapter in "Developments in the Structural Chemistry of Alloy Phases" [1967 Symposium, The Metallurgical Society (AIME), Cleveland, Ohio], Plenum Press, in press.
- W. B. Pearson and C. B. Shoemaker, "A System of Coding and Generating of Layered, Tetrahedrally Close-Packed Structures", *Acta Cryst.*, in press.

X. MOLECULAR CRYSTALS

Faculty:

R. J. Silbey, Assistant Professor, Chemistry

Graduate Students:

M. Grover, NASA Trainee, Chemistry

P. Chalmer, NSF Predoctoral Fellow, Chemistry

J. Schroeder, Teaching Assistant (Fall 1967), Chemistry, Research Assistant (Spring 1968, Summer 1968)

M. Christine Scheid, Teaching Assistant, Chemistry

Judith Herzfeld, NSF Predoctoral Fellow, Chemistry

S. Rackovsky, Woodrow Wilson Fellow (Fall 1967 - Spring 1968)
NSF-Predoctoral Fellow (Summer 1968), Chemistry

Sponsorship:

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

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

Petroleum Research Fund of American Chemical Society,
PRF # 3574-A5 (from September 1, 1968)

Research Report

During the past year, research was started on a number of topics relating to the theoretical study of the energy levels and spectral properties of molecular crystals.

The description of the electronic energy levels of molecular crystals on the basis of the Frenkel model is known to be very restrictive. We have begun research on the effect of introducing ion-pair states into the formalism. Recent approximate work on the aromatic hydrocarbons has shown that these ion pair states may play a significant role in the description of states which have small oscillator strength. The present work is concerned with solving simplified model problems analogous to the above.

Progress has been made on the description of the exciton-phonon interaction in molecular crystals. We have shown that the Green's function methods previously used may be in serious error. Perturbation

and variational methods are being used to find the approximate self energies of the coupled exciton-phonon system.

During the past year, a re-examination of the theoretical interpretation of the spectra of crystalline benzene and naphthalene was completed. It was shown that in order to theoretically predict all the experimental data, one must allow for ion-pair states to be mixed into the Frankel exciton states. When this is done, good agreement is obtained.

Publications

W. Greer, S. A. Rice, J. Jortner and R. Silbey, "A Re-examination of the Theoretical Interpretation of the Spectra of Crystalline Naphthalene and Benzene" J. Chem. Phys. 48, 5667 (1968).

XI. MOLECULAR SPECTROSCOPY

Faculty:

R. C. Lord, Professor, Chemistry

Research Staff:

R. F. Lake, Research Associate, Chemistry

I. Harada, Research Associate, Chemistry

D. W. Wertz, Research Associate, Chemistry

Graduate Students:

C. C. Milionis, Research Assistant, Chemistry

W. J. Adams, Research Assistant, Chemistry

T. L. Berman, Research Assistant, Chemistry

L. A. Carreira, Research Assistant, Chemistry

D. C-M. Luk, Research Assistant, Chemistry

C. W. Wickstrom, Research Assistant, Chemistry

Nai-teng Yu, Norris Research Fellow, Chemistry

C. S. Blackwell, Teaching Assistant, Chemistry

R. Mendelsohn, Teaching Assistant, Chemistry

Support Staff:

Ruth C. Deininger, Secretary, Chemistry

Sponsorship:

Spectroscopy Laboratory: National Science Foundation, GP-4923-X2,
DSR 70956

Spectroscopy Laboratory: National Institutes of Health, 1 RO1 GM15310-
02 BBCB, DSR 71166

Research Report1.0 Studies in Far Infrared Spectroscopy1.1 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. For example, the chair and boat forms of cyclopentene epoxide are found to have an energy difference of about 0.3 kcal/mol and a barrier to inversion of 2 kcals/mol.

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 9-10 kcal.

In addition to inversion, the phenomenon of pseudo-rotation is currently under investigation in various five- and six-membered rings such as cyclopentanone, tetrahydrothiophene and dihydropyran. The supposedly linear molecule carbon suboxide has also 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 $20\text{--}80\text{ cm}^{-1}$ and the interpretation of the data is in progress.

1.2 Pure Rotational Far Infrared Spectra

The extensive study made by Dr. G. O. Neely of the pure rotational spectra of HN_3 and related compounds has now appeared in print (see "Publications"). No other work on pure rotational spectra is currently in progress.

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 the 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:

None

Publications:

- J. Laane and R. C. Lord, "Far Infrared Spectra of Ring Compounds. II: Spectrum and Ring Puckering Potential of Cyclopentene", J. Chem. Phys., 47, 4941 (1967).
- J. Laane and R. C. Lord, "Far Infrared Spectra of Ring Compounds. III: Spectrum, Structure and Ring-Puckering Potential of Silacyclobutane", J. Chem. Phys., 48, 1508 (1968).
- T. M. Hard and R. C. Lord, "A Double-Beam High-Resolution Spectrometer for the Far Infrared", Applied Optics 7, 589 (1968).
- B. Krakow, R. C. Lord and G. O. Neely, "A High-Resolution Far-Infrared Study of Rotation in HN_3 , HNCO , HNCS and Their Deuterium Derivatives", J. Mol. Spectry. 27, 148 (1968).
- G. O. Neely, "Interpretation of Extreme Centrifugal Distortion in HNCO , HNCS and Their Deuterium Derivatives", J. Mol. Spectry. 27, 177 (1968).

- R. C. Lord and G. J. Thomas, Jr., "Spectroscopic Studies of Molecular Association in DNA Constituents", *Developments in Appl. Spectroscopy*, vol. 6, pp. 179-199, Plenum Press, 1968.
- Y. Kyogoku, R. C. Lord and A. Rich, "The Specific Hydrogen Bonding of Barbiturates to Adenine Derivatives", *Nature* 218, 69-72 (April 6, 1968).
- 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* (in press).
- R. C. Lord and W. C. Pringle, Jr., "A Search for Pure Rotational Absorption in Allene", *J. Chem. Phys.* (in press).

XII. INFRARED AND RAMAN SPECTROSCOPY OF SOLIDS

Faculty:

C. H. Perry, Assistant Professor, Physics

Research Staff:

Dr. R. P. Lowndes, DSR Staff, Research Laboratory of Electronics

Graduate Students:

Jeanne H. Fertel, Graduate Assistant, Physics

D. J. Muehlner, National Science Foundation Fellow, Physics

K. Owyang, Undergraduate Assistant, Physics

J. F. Parrish, National Science Foundation Fellow, Physics

N. E. Tornberg, Graduate Assistant, Physics

Personnel who have left:

C. H. Perry, Assistant Professor, Physics (Now Associate Professor, Physics Department, Northeastern University, Boston, Massachusetts)

R. P. Lowndes, DSR Staff, Research Laboratory of Electronics (Now Assistant Professor, Physics Department, Northeastern University, Boston, Massachusetts)

D. J. Muehlner, National Science Foundation Fellow, Physics (To Gravitation Research, R. L. E., MIT)

K. Owyang, Undergraduate Assistant, Physics

Degrees Granted:

Jeanne H. Fertel, Ph.D., Physics, January 1969

J. F. Parrish, Ph.D., Physics, January 1969

N. E. Tornberg, Ph.D., Physics, January 1969

K. Owyang, S.B., Physics, June 1968

Sponsorship:

Research Laboratory of Electronics, supported in part by the Joint Services Electronics Program under Contract DA28-043 AMC-02536 (E), DSR 70050

Air Force Cambridge Research Laboratories, AF 19(628)-6066, DSR 70121

National Aeronautics and Space Administration, Grant NGR 22-009-(237), DSR 70988
Spectroscopy Laboratory. Supported in part by the National Science Foundation, Grant Number GP-4923, DSR 76049. Optical Equipment Grant: MIT Sloan Fund for Basic Research.

Research Report

The activities of this group have been concentrated on the study of collective oscillations in solids determined by both infrared and Raman spectroscopy. A number of projects are still in progress and will be submitted for publication.

In September, 1968, the Infrared and Raman spectroscopy of solids group moved to the Physics Department, Northeastern University, Boston, Massachusetts. The progress up to this time can be summarized by the publications and papers presented at various international meetings during the year.

1.0 Optical Phonons and Symmetry of Tysonite Lanthanide Fluorides

Personnel: C. H. Perry; R. P. Lowndes, J. F. Parrish

Research Report:

The polarized infrared reflectance of LaF_3 , CeF_3 , PrF_3 , and NdF_3 has been measured from 40 cm^{-1} to 500 cm^{-1} at 295°K , 78°K , and 7°K . Kramers-Kronig analyses of the reflectance spectra yield evidence for eleven infrared active phonons in the σ -polarization ($\vec{E} \perp c$) and six in the π -polarization ($\vec{E} \parallel c$). These results, together with reported magnetic resonance measurements, are consistent with a $\text{P}\bar{3}'c'1$ magnetic space group. A theory and method for directly observing the longitudinal optical (LO) phonon frequencies of strongly anisotropic crystals in transmission is reported.

2.0 Far Infrared Electronic Transitions in Tysonite Rare-Earth Fluorides

Personnel: J. F. Parrish, R. P. Lowndes and C. H. Perry

Research Report:

Electronic transitions between the crystalline Stark levels of the ground state manifold of Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Er^{3+} held in LaF_3 , CeF_3 , PrF_3 and NdF_3 host lattices have been investigated using far infrared spectroscopy. No transitions were observed between $40\text{-}100\text{ cm}^{-1}$ for either the Ce^{3+} or Sm^{3+} ions held in the various host lattices, a factor in contradiction to energy level schemes predicted from previous fluorescence and optical absorption measurements. Low energy ($40\text{-}100\text{ cm}^{-1}$) electronic transitions between the ground state and first excited states of the $^3\text{H}_4$ Pr^{3+} , $^4\text{I}_{9/2}$ Nd^{3+} and $^4\text{I}_{15/2}$ Er^{3+} Stark multiplets have been observed and the Zeeman splitting of these transitions have been studied in magnetic fields up to 150 kilogauss.

3.0 The Phonon Spectra and Phase Transitions in the Ammonium Halides

Personnel: C. H. Perry; R. P. Lowndes

Research Report:

The infrared and Raman lattice spectra of several ammonium halides have been investigated as a function of temperature from $4\text{-}300^\circ\text{K}$. One infrared active (reststrahlen) mode is observed in the disordered cubic phase. In the ordered cubic phase for NH_4Cl , ND_4Cl (phase III) and NH_4Br , ND_4Br (phase IV), the main lattice mode is simultaneously infrared and Raman active. The temperature dependence of the frequency and damping constant has been studied extensively using both techniques. In the tetragonal phase (D_{4h}^7 ($\text{P4}/\text{mmm}$)) for NH_4Br , ND_4Br and NH_4I (phase III), five bands are observed in the Raman spectrum corresponding to the four translational modes and one vibrational mode. The infrared spectrum shows only one translational lattice mode. The frequencies and symmetries of the $k \approx 0$ allowed modes in the various phase transitions have been obtained. The nature of the interatomic interactions governing the extent of the ionic distortions and the compressibilities of these solids has been studied.

4.0 The Temperature Dependent Phonon Spectrum of PbTiO_3

Personnel: C. H. Perry; N. E. Tornberg

Research Report:

The frequencies and symmetries of the allowed $k \approx 0$ transverse and longitudinal modes were obtained from a Kramers-Kronig analysis of far infrared reflectance data taken between 80-800°K. Above the Curie temperature (760°K), PbTiO_3 exhibits a broad second order Raman spectrum. Below this temperature - in the ferroelectric tetragonal phase - a first order spectrum is superimposed which increases in strength as the temperature is lowered. The bands in PbTiO_3 observed just below T_c at about 65, 120, 185, 280 and 495 cm^{-1} show a shift of approximately 4, 5, 8, 2 and 3.5 cm^{-1} per 100°K, respectively, to higher frequency as the temperature is lowered. The relative contributions of the various modes to the dielectric dispersion indicates that the lowest frequency E_u mode is the "softest". Other modes of the same symmetry also contribute significantly to the temperature dependence of ϵ_0 and they may also approach some type of instability in the paraelectric phase.

5.0 Optical Phonons in $\text{KCl}_{1-x}\text{Br}_x$ and $\text{K}_{1-x}\text{Rb}_x\text{I}$ Mixed Crystals

Personnel: J. H. Fertel and C. H. Perry

Research Report:

The infrared lattice-vibrational spectra of mixed crystals of $\text{KCl}_{1-x}\text{Br}_x$ and $\text{K}_{1-x}\text{Rb}_x\text{I}$ have been observed at temperatures down to 80°K. The results were obtained from thin-film transmission measurements and Kramers-Kronig analyses of reflection data. A classical oscillator model was used to fit the reflectivity curves for the pure end members. The $\text{KCl}_{1-x}\text{Br}_x$ system shows the normal 'one-mode' behavior. Two infrared active phonons occur in the $\text{K}_{1-x}\text{Rb}_x\text{I}$ system and is the first observation of this type of behavior in an alkali halide mixed crystal. The applicability of several theoretical models and the various criteria for one and two mode behavior have been evaluated.

6.0 Optical Phonons in Mixed Sodium Potassium Tantalates

Personnel: C. H. Perry; N. E. Tornberg

Research Report:

The infrared and Raman spectra of members of the mixed crystal system $(\text{Na}_x\text{K}_{1-x})\text{TaO}_3$ have been studied at temperatures from 4 to 600°K for $x = 0.0, 0.12, 0.40, 0.65$, and 0.85 . The infrared data have been used to interpret the first order Raman data, and to follow the ferroelectric "soft" mode and verify the compatibility of its behavior with that predicted by the theory of displacive ferroelectrics. The Raman spectra have been examined in the paraelectric phase where they are entirely second order for most samples, in the ferroelectric phase where there are superimposed first order spectra, and in the region of the phase transition. Optical mode frequencies at the center and edge of the Brillouin zone have been tabulated as a function of temperature and composition.

7.0 The Phonon Spectra and Phase Transitions in the $\text{K}(\text{Ta:Nb})\text{O}_3$ Mixed Crystal System

Personnel: C. H. Perry; N. E. Tornberg

Research Report:

Solid Solutions of $\text{K}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_3$ have been studied by means of far infrared and Raman spectroscopy for $x = 0.0, 0.25, 0.65, 0.89$ and 1.0 . Members of this series exist in cubic, tetragonal, orthorhombic and rhombohedral phases at successively lower temperatures in the range 10-800°K except KTaO_3 which remains cubic. In the paraelectric (cubic) phase these materials exhibit a strong infrared reflectance spectrum and a second order Raman spectrum similar to KTaO_3 . The infrared spectra are relatively unaffected through the various ferroelectric phase transitions but the Raman spectra exhibit strong first order bands which alter markedly at each structural change. Considerable hysteresis is observed in the spectra at most transitions. The infrared measurements provided a starting point for the interpretation of the Raman spectra and assignments of the phonon modes in each phase as a function of composition will be reported.

8.0 Dielectric Response of the Alkaline Earth Fluoride

Personnel: R. P. Lowndes

Research Report:

The temperature dependence of the low-frequency dielectric response of CaF_2 , SrF_2 and BaF_2 over the range $2^\circ\text{--}350^\circ\text{K}$ is reported, together with the pressure dependence, for hydrostatic pressures up to 5 kilobars, at selected temperatures in the range $60^\circ\text{--}350^\circ\text{K}$. The low-temperature data are used to assess the nature and extent of the electronic structure and interionic forces of the alkaline earth fluorides. The temperature dependence of the dielectric response is found to be due principally to intrinsic volume changes in the crystals rather than to intrinsic temperature changes in the self-energy. The quasi-harmonic contributions are analyzed to determine values of 2.58, 2.44 and 2.53, respectively, for CaF_2 , SrF_2 and BaF_2 for the $k \approx 0$ infrared active one-phonon Gruneisen constants. The temperature dependence under constant volume of the self-energy contribution to the dielectric constant of all three salts exhibits a maximum value near $0.25 \theta_D$ where θ_D is the characteristic Debye temperature.

Publications:

- R. P. Lowndes, J. F. Parrish and C. H. Perry, "Optical Phonons in Tysonite Rare-Earth Fluorides", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 56, paper L1.
- J. F. Parrish, R. P. Lowndes and C. H. Perry, "Far Infrared Electronic Transitions in Tysonite Rare-Earth Fluorides", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 26, paper L2.
- J. H. Fertel, K. Owyang and C. H. Perry, "Observation of Two-Mode Behavior in an Alkali Halide Mixed Crystal System", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 57, paper L3.
- R. P. Lowndes and D. H. Martin, "Temperature Dependence Under Constant Volume of Lattice Resonance in Ionic Solids", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 57, paper L4.
- C. H. Perry and N. E. Tornberg, "The Temperature Dependent Phonon Spectrum of PbTiO_3 ", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 57, paper L5.
- N. E. Tornberg and C. H. Perry, "The Phonon Spectra and Phase Transi-

- tions in the $K(\text{Ta:Nb})\text{O}_3$ Mixed Crystal System", Proc. Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 3-7, 1968, p. 57-8, paper L6.
- C. H. Perry and N. E. Tornberg, "Raman Spectra of PbTiO_3 and Solid Solutions of NaTaO_3 - KTaO_3 and KTaO_3 - KNbO_3 ", Proc. International Conference on Light Scattering Spectra of Solids, September 3-6, 1968; ed. G. B. Wright, Springer-Verlag, New York, 1969, paper F-3. Solid State Comm. 6, XVI (1968).
- R. P. Lowndes, "Dielectric Response of the Alkaline Earth Fluorides", (submitted to Proc. Phys. Soc., London).
- J. H. Fertel and C. H. Perry, "Optical Phonons in $\text{KCl}_{1-x}\text{Br}_x$ and $\text{K}_{1-x}\text{Rb}_x\text{I}$ Mixed Crystals (submitted to Phys. Rev.).
- C. H. Perry and N. E. Tornberg, "Optical Phonons in Mixed Sodium-Potassium Tantalates" (submitted to Phys. Rev.).
- R. P. Lowndes, J. F. Parrish and C. H. Perry, "Optical Phonons and Symmetry of Tysonite Lanthanide Fluorides" (submitted to Phys. Rev.).
- J. F. Parrish, R. P. Lowndes and C. H. Perry, "Far Infrared Electronic Transition of Nd^{3+} in Tysonite Lanthanide Fluorides" (submitted to Physics Letters).

XIII. MICROWAVE SPECTROSCOPY

Faculty:

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

Research Staff:

J. G. Ingersoll, DSR Staff, Research Laboratory of Electronics
J. D. Kierstead, DSR Staff, Research Laboratory of Electronics
S. R. Reznick, DSR Staff, Research Laboratory of Electronics

Graduate Students:

J. B. Barton, Teaching Assistant and Research Assistant, Physics
J. Berman, Research Assistant, Physics
R. L. Espino, Research Assistant, Chemical Engineering
L. R. Fox, Research Assistant, Physics
J. U. Free, Research Assistant, Physics
R. M. Langdon, Jr., Research Assistant, Physics
M. K. Maul, Research Assistant, Electrical Engineering
B. Yung, Research Assistant, Physics
G. Rappe, Doctoral Thesis Student, Chemical Engineering
R. Olsen, Master's Thesis Student, Electrical Engineering
Shirley Jackson, Graduate Student, Physics
P. Bente, Undergraduate Thesis Student, Chemical Engineering
B. A. Eisenstat, Undergraduate Thesis Student, Physics
C. B. Friedberg, Undergraduate Thesis Student, Physics
S. R. Kutner, Undergraduate Thesis Student, Physics
M. J. Markovitz, Undergraduate Thesis Student, Physics
R. Woerner, Undergraduate Thesis Student, Physics

Support Staff:

R. Hartman, Student Employee, Economics
W. J. Schwabe, Senior Technician, Research Laboratory of Electronics
Irene A. Olasz, Secretary, Research Laboratory of Electronics

Personnel who have left:

R. Espino (Now at Chemical Systems, Inc., New York)

M. K. Maul (Now at Bell Telephone Laboratories, Murray Hill,
New Jersey)
R. Olsen (Now at Honeywell Corporation)
S. R. Reznek (Now at the Technical University in Denmark)

Degrees Granted:

M. K. Maul, Ph.D., Electrical Engineering, August 1968
R. E. Espino, Sc.D., Chemical Engineering, February 1968
R. E. Olsen, S.M., Electrical Engineering, January 1968
C. B. Friedberg, B.S., Physics, June 1968
M. J. Markovitz, B.S., Physics, June 1968
S. R. Kutner, B.S., Physics, August 1968

Sponsorship:

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

Research Report

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

1.0 Metals

Personnel: M. W. P. Strandberg, R. L. Kyhl; J. B. Barton, B. N. Yung,
R. M. Langdon

The electronic structure of Ga, Cu, Sn is being measured using a
technique which observes the variation of electromagnetic surface impedance
of a metal single crystal at low temperatures with applied magnetic field.
Theoretical studies have been carried out to investigate the transport
properties of these crystals under the conditions imposed by the experiment.
Past results on Ga indicate that APW band calculations of its Fermi surface
are essentially correct. Present emphasis is towards understanding
surface impedance variation with small (0-100g) imposed magnetic field in
the hope of extracting information on the temperature and wave vector
dependence of electron mean free paths.

2.0 Electron Paramagnetic Resonance

Personnel: M. W. P. Strandberg; G. Rappe

This work is mainly interdisciplinary. Research in cooperation with the Chemical Engineering Department has measured the reaction rate constant for atomic hydrogen reacting with solid propylene. The mechanics of the reaction have also been tentatively defined. A study is being made of the mechanism of electric conduction in protein molecules using the EPR apparatus to detect magneto-resistance effects.

3.0 Ultrasonics

Personnel: M. W. P. Strandberg; J. U. Free, L. R. Fox, R. Woerner

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

4.0 Superconducting Bolometers

Personnel: M. W. P. Strandberg, R. L. Kyhl; M. K. Maul

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

The noise properties of some tin superconducting thin film bolometers have been measured. Resistance fluctuations are one or two orders of magnitude larger than that predicted by thermodynamics for temperature fluctuations.

This excess noise is largely eliminated by application of a weak perpendicular magnetic field (~ 10 gauss).

A theory of the incremental electrical impedance of superconducting bolometers has been developed. Among other things, it allows one to determine the thermal time constant of these devices from r.f. measurements of the impedance of the bolometer.

Theses:

- M. K. Maul, "Excess Noise in Superconducting Bolometers," Ph. D. Thesis, Department of Electrical Engineering, August 1968.
- R. L. Espino, "The Reaction of Atomic Hydrogen with Solid Olefin Films at Cryogenic Temperatures," Sc. D. Thesis, Department of Chemical Engineering, February 1968.
- R. E. Olsen, "Heterodyne Detection Characteristics of Josephson Functions," S.M. Thesis, Department of Electrical Engineering, January 1968.
- C. B. Friedberg, "Microwave Magnetoresistance Measurements," B. S. Thesis, Department of Physics, June 1968.
- M. J. Markovitz, "Electronic Contribution to Ultrasonic Attenuation in a Metal Film," B.S. Thesis, Department of Physics, June 1968.
- S. R. Kutner, "Electron Spin Resonance Absorption of Perylene," B.S. Thesis, Department of Physics, August 1968.

Publications:

- J. M. Andrews and M. W. P. Strandberg, "Effect of Phonon Dispersion on Heat Pulse Shape," Phys. Rev. 173, 3, pp. 869-872 (1968).
- R. L. Kyhl, "Fast Sensitive Smith Chart Plotter or Microwave Reflectometer," RSI 39, 3, pp. 373-376 (1968).
- R. L. Espino, J. J. Jones, R. C. Reid, and M. W. P. Strandberg, "Interruption and Evaporation Effects for the Reaction of Atomic Hydrogen with Solid Olefins at 77°K," J. of Phys. Chem. 72, 3689 (1968).

Papers submitted for publication:

- M. W. P. Strandberg, "Superconducting Bolometers: Detection of Ambient Acoustic Noise," Transaction of the Conference on Fluctuations in Superconductors.
- R. L. Espino, R. C. Reid, and M. W. P. Strandberg, "The Reaction of Atomic Hydrogen with Solid Olefin Films at Cryogenic Temperatures," Journal of Chemical Physics.
- C. B. Friedberg and M. W. P. Strandberg, "Microwave Magnetoresistance Measurements," Journal of Applied Physics.
- S. R. Reznick and M. W. P. Strandberg, "Surface Impedance for a Simple Metal Under Conditions of Radio-Frequency Size Effect," Phys. Review.
- S. R. Reznick and M. W. P. Strandberg, "Radio-Frequency Transport for a Simple Metal in a Magnetic Field," Physical Review.

- M. K. Maul, M. W. P. Strandberg, and R. L. Kyhl, "Excess Noise in Superconducting Bolometers," *Physical Review*.
- M. K. Maul and M. W. P. Strandberg, "Equivalent Circuit of a Superconducting Bolometer," *Journal of Applied Physics*.
- R. L. Espino, "Reaction of Atomic Hydrogen with Solid Olefin Films at Cryogenic Temperatures," *QPR 88*, pp. 11-12, Research Laboratory of Electronics, MIT, January 15, 1968.
- (The following are abstracts of theses published in the R. L. E. Quarterly Progress Report):

- S. R. Reznick, "The Radio-Frequency Size Effect in Anomalous Skin Depth Region," *QPR 88*, pp. 11-12, Research Laboratory of Electronics, MIT.
- C. B. Friedberg, "Microwave Magnetoresistance Measurements," *QPR 90*, p. 7, Research Laboratory of Electronics, MIT.
- M. J. Markovitz, "Electronic Contribution to Ultrasonic Attenuation in a Metal Film," *QPR 90*, pp. 7-8, Research Laboratory of Electronics, MIT.
- S. R. Kutner, "Electron Spin Resonance Absorption of Perylene," *QPR 91*, p. 1, Research Laboratory of Electronics, MIT.
- M. K. Maul, "Excess Noise in Superconducting Bolometers," *QPR 91*, pp. 1-2, Research Laboratory of Electronics, MIT.

Meeting papers presented during 1968:

- M. W. P. Strandberg and S. R. Reznick, "Surface Scattering and the Radio-Frequency Size Effect," presented at the Statler Hilton Hotel, Boston, Massachusetts, February 26-28, 1968.
- S. R. Reznick and M. W. P. Strandberg, "Surface Impedance and Boundary Scattering in Metals," presented at the 11th International Conference on Low Temperature Physics, St. Andrews, Fife, Scotland, August 25-28, 1968.
- M. W. P. Strandberg, "ESR Line Shapes" and Statistical Theory of Line Shapes," presented at the Summer School on Radio-Frequency Spectroscopy, Perugia, Italy, August 26-September 14, 1968.
- M. W. P. Strandberg and S. R. Reznick, "Mean Free Path Determination by Surface Scattering," presented at the Eidgenossische Technische Hochschule, Zurich, Switzerland, September 3-5, 1968.
- M. W. P. Strandberg, "Surface Magneto-Resistance of Metals at Low Temperatures," presented at Wayne State University, Detroit, Michigan, November 21, 1968.

XIV. OPTICAL AND INFRARED LASERS

Faculty:

- A. Javan, Professor, Physics
- A. Szoke, Associate Professor, Physics
- M. Feld, Assistant Professor, Physics
- R. Brewer, Visiting Professor, Physics
- G. Koppelman, Visiting Associate Professor, Physics

Research Staff:

- P. Bonczyk, DSR Staff, Physics
- V. Daneu, DSR Staff, Physics
- L. Hocker, DSR Staff, Physics
- S. Iwasa, DSR Staff, Physics
- N. Kurnit, Research Associate, Physics
- J. Lifshitz, DSR Staff, Visiting, Physics

Graduate Students:

- T. Ducas, Research Assistant, Physics
- B. Feldman, Research Assistant, Physics
- H. Grieneisen, Brazilian Fellowship, Physics
- M. Kelly, Research Assistant, Physics
- M. Kovacs, Research Assistant, Physics
- J. Levine, Research Assistant, Physics
- F. Missell, Research Assistant, Physics
- J. Murray, Research Assistant, Physics
- C. Rhodes, Research Assistant, Physics
- A. Sanchez, Research Assistant, Physics
- J. Small, Research Assistant, Physics
- D. Sokoloff, NSF Fellowship, Physics

Support Staff:

- L. Ryan, Jr., Engineering Assistant, Physics
- R. Solomon, Administrative Assistant, Project Administrator, Physics
- Jennifer Lewis, Secretary, Physics
- Ellen O'Toole, Secretary, Physics

Personnel who have left:

- P. Bonczyk, DSR Staff, Physics (Now at University of Bonn, Germany)
- J. Parks, DSR Staff, Physics (Now at University of Southern California, Los Angeles, California)
- D. Ramachandra Rao, Visiting Scientist, Physics (Now at Indian Institute of Technology, Kanpur, India)
- P. Schroeder, Research Assistant, Physics (Now at Bell Telephone Laboratory, Allentown, Pennsylvania)

Degrees Granted:

- J. Parks, Ph.D., Physics, September 1968

Sponsorship:

- National Aeronautics and Space Administration, NGL-22-009-012, DSR 76148; NGR-22-009-240, DSR 70382
- Air Force Cambridge Research Laboratories F19(628)-67-C-0074, DSR 70140; F19(628)-68-C-0204, DSR 70898
- Office of Naval Research Nonr-3963(22), DSR 74979; 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 utilizing various gas lasers. The group's activities encompass a broad range of the electro-magnetic spectrum -- from submillimeter wavelengths and the far infrared, to the short wavelength ultraviolet. Attempts are being made to introduce a unified approach in exploring a varied set of problems. This approach requires development of vastly different technologies where fundamental research objectives have, by necessity, evolved together with development of related problems in applied research. The various activities of the group may be subdivided into several broad categories each consisting of several experiments:

- 1.0 Molecular Relaxation Studies
- 2.0 Application of a Laser Magnetoreflexion Spectrometer to a High Resolution Study of Graphite, Bismuth, and Antimony
- 3.0 Transmission Behavior of a Short Light Pulse
- 4.0 High Resolution Studies Utilizing Laser-Induced Line Narrowing Effects

- 5.0 Absolute Frequency Measurements and Experiments in the Infrared and Far Infrared
- 6.0 Other Gas Laser Experiments

1.0 Molecular Relaxation Studies

A number of techniques have been developed and applied to studies of collisional coupling between various vibrational states in CO_2 molecules. A variety of molecular vibrational relaxation and excitation transfer effects have already been explored in detail. The study of CO_2 has been emphasized since it is believed that a detailed knowledge of various collisional processes occurring in the same molecule provides an important basis for tests and further development of suitable theories. Furthermore, such studies provide information directly relevant to the functioning and ultimate performance expectation of high-power molecular gas lasers.

In these studies, a sudden change in population of a specific CO_2 level is induced by applying the output of a repetitive Q-switched laser pulse to an external cell containing CO_2 molecules at room temperature. After each Q-switched pulse the excitation transfer to other vibrational levels and the subsequent decay back to the equilibrium state is observed and studied in several ways. To facilitate the measurements, a multichannel analyzer is used for storage and averaging of the time behavior information of repetitive decaying signals. This technique provides great sensitivity for observation of otherwise weak signals. Measurements are done on volume quenching rates, diffusion of 001 vibrational states and its wall deactivation probability. (It is found that the diffusion constant for 001 diffusion through CO_2 is different than the known constant for self diffusion of CO_2 .) Relaxation of 100 state is also determined in considerable detail. In another experiment, pressure dependence of the imprisoned spontaneous decay rate of 001 state arising from 4.35μ ($001 \rightarrow 000$) transition is determined over a wide pressure range; the results are compared with theory.

2.0 Application of a Laser Magnetoreflexion Spectrometer to a High Resolution Study of Graphite, Bismuth, and Antimony

An infrared laser, which employs 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, bismuth (Bi) and antimony (Sb). 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. In addition, a technique is developed to obtain the first and second derivative of reflectivity with respect to the magnetic field ($\delta R/\delta H$ and $\delta^2 R/\delta H^2$). Thus 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 (conducted in close collaboration with Professor M. Dresselhaus), it is found that the carriers at point K in the Brillouin zone are electrons rather than holes. This has brought about a rather significant change in the graphite band-model.

In the study of Bi, the derivative spectra $\delta R/\delta H$ of the oscillatory interband reflection in the Faraday configuration has been investigated in two orientations; the one in which the field and the laser poynting vector are parallel to the binary axis, and the other to the bisectrix axis. The critical field values corresponding to the sharp peaks, which represent the resonance condition for allowed interband transitions with the selection rule of $\Delta n = 0$ and $\Delta m = \pm 2$, have been fitted with the two band model proposed by Lax. The agreement is good for low photon energies and for low quantum transitions, however, an increasingly worse deviation is seen for high photon energies, indicating the inadequacy of the simple two band model. The presence of nearby bands which interact with the mirror bands proposed by Baraff, is further evidenced by the striking doublet structure. The spin degeneracy of the conduction and valence bands are lifted by different amounts depending on the relative location of the third band, and the observed splitting is interpreted to give the difference. Since transport measurements have established the conduction band splitting of the order of 10% of the Fermi energy, the present measurement provides the hitherto inaccessible valence band splitting. A theory along the line proposed by Baraff is under way. Of the two series of oscillations observed for the bisectrix direction, the one associated with the non-principal ellipsoid (heavy mass) exhibits a marked polarization dependence. This dependence which is related to the ellipsoidal profile on the trigonal-binary plan has been measured with accuracy. The sharpness of the spectra derives itself from the monochromaticity of the laser light. An unexpected byproduct is the first such quantitative measurement of the temperature dependence of the Landau level spacing and the associated relaxation time between 77K and 4K.

In the case of Sb, the optical Shubnikov-de Haas effect is investigated using laser radiation at 10.978μ , 11.29μ , and 11.89μ . The effect manifests itself as oscillations in the optical conductivity which are periodic in $(1/H)$, as is characteristic of the deHaas-van Alphen type measurements. The

phenomenon hinges 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. The laser spectrometer with its fine focussability and small aperture satisfies all these conditions and indeed, the oscillatory amplitudes of at least ten times as large as those of conventional optics have been recorded. In the meantime, a simple theory involving a degenerate parabolic conduction band with an isotropic mass has been developed. Simulating the case of laser photon energies of 0.090 eV, 0.095 eV, and 0.105 eV being incident on the Sb binary face, the computation at $T = 0$ K with parameters of $\hbar\omega_1 = 0.100$ eV, $m = 0.073m_0$ and $\tau = 1.0 \times 10^{-13}$ sec has predicted the main qualitative feature of the observed phenomena, namely a) the period, b) the asymmetry and c) the reversal of the line shape about the plasma frequency. The calculation is being extended to incorporate finite temperatures and a more realistic Sb band model. This experiment is done also in close collaboration with Professor M. Dresselhaus.

3.0 Transmission Behavior of a Short Light Pulse

It is known that under appropriate conditions an electromagnetic light pulse can propagate undistorted and without energy loss through a normally absorbing medium. Specifically, this "self-induced transparency effect" was initially discussed and demonstrated by McCall and Hahn for the case of an absorbing medium consisting of a single pair of energy levels forming a nondegenerate transition. In a recent theoretical analysis we have shown that the self-induced transparency effect is considerably modified when there are several pairs of levels with overlapping transition frequencies and matrix elements of different values. An important example is that of dipolar transitions between states having angular momentum quantum numbers j and j' or both are greater than one. In the absence of a Stark or Zeeman perturbation, the magnetic sublevels m_j (or $m_{j'}$) are degenerate and the dipole matrix elements $\mu_{jj'm_jm_{j'}}$ depend on m_j and $m_{j'}$. We find, for instance, that the pulse shape and its propagation behavior depend strongly on the angular momentum quantum numbers associated with the transition. The results show that an undistorted propagating pulse solution of finite energy may only exist for $j \neq j'$ (arbitrary $j > 0$) in addition to the special cases $0 \neq 1$ and $1/2 \neq 3/2$. The steady state pulse shape in the $j \neq j'$ case is multiply peaked with j maxima for integer j and with $j + 1/2$ maxima for half integer j . (For a transition $0 \neq 1$ or $1/2 \neq 3/2$ the pulse has a single maximum.) A finite energy, zero degree pulse defined as $\int_{-\infty}^{\infty} \mathcal{E}(z, t) dt = 0$ is also found to

propagate without energy loss although not without distortion. This is true for arbitrary j for both $j \neq j \pm 1$ and $j = j$.

The above transparency results for $J \neq J$ with $J > 1$ and for a zero degree pulse is shown to hold rigorously in the absence of an inhomogeneous broadening and for pulse carrier frequency at the center frequency of the absorption line. It is shown further, that the effect of inhomogeneous broadening tends to introduce loss terms for $j \neq j$ transitions with $J > 1$ and also for a zero degree pulse. However, a detailed analysis, using computer calculation, shows that the general propagation behavior described above is maintained to a large extent even in the presence of an inhomogeneous broadening, e. g., for a $J \neq J$ transition, there exist multiply peaked pulse solutions of the type described above, such that the corresponding attenuation factor is considerably below that of an arbitrary pulse saturating the atomic resonance.

In an earlier publication by Patel and Slasher, it was reported that gaseous SF_6 provides an unidentified absorption resonance at one of the P-branch transitions at 10.6μ which shows a self-induced transparency effect similar to the one observed earlier by Hahn and McCall in ruby. We find, however, that the absorption in SF_6 is of the type that cannot admit self-induced transparency. On the other hand, the SF_6 resonance has provided an excellent means of studying the important questions regarding transmission of a short pulse; a number of such experiments have been performed and the results compared with theory.

4.0 High Resolution Studies Utilizing Laser-Induced Line Narrowing Effects

A major interest of the MIT laser group in the studies of the nonlinearities of atomic transitions has been resonant processes which produce linewidth changes considerably narrower than the normal Doppler widths (or in general, the inhomogeneous widths) of optical spectral lines. These processes provide important means for high-resolution studies of the structure of atomic transitions which are completely overlapping and ordinarily unresolvable. Several effects of this type have been explored in considerable theoretical detail; the predictions have been tested and utilized in precision spectroscopic determinations such as the isotope shifts, fine and hyperfine splittings. So far, various spectroscopic applications have been confined to transitions between atomic states in gases. Experiments are being planned to extend these techniques to paramagnetic levels of impurity-

doped solids. Both aspects have been subjects of detailed experimental and further theoretical studies.

There exists an additional effect which may also be classified under the "laser-induced line narrowing effect;" this additional effect, to be referred to as the "stimulated level-crossing effect," is an induced version of the well-known level crossing effect observed previously in spontaneous emission from atoms pumped by a broad-band source. In the stimulated level-crossing effect, one is concerned with the transmission of an intense monochromatic light through a gas possessing a Doppler broadened resonance with closely spaced structure. The effect manifests itself as a "non-linear" change in the induced polarization as appropriate pairs of tunable atomic levels are made to overlap within their natural widths. This results in a change in the transmission coefficient, i. e., gain or attenuation of the incident radiation when the level crossing occurs. The "stimulate level-crossing effect" is observed and applied in detailed precision studies of hyperfine structure in an excited electronic state of Xe^{129} .

5.0 Absolute Frequency Measurements and Frequency Mixing Experiments in the Infrared and Far Infrared

The activities of the Group in the area of frequency mixing and multiplication have lead to the development of new types of infrared (IR) and far infrared (far IR) frequency mixers and rectifiers consisting of special types of fast-response point-contact diodes. These diodes are utilized as circuit elements at high IR frequencies in much the same way as ordinary diodes are used at low frequencies. The realization of these diodes has required the development of micromanipulation and special microcircuitry techniques necessitated by the short IR wavelengths. For instance, we are able to couple linearly polarized 10μ IR radiation into a thin wire antenna having a diameter of about 2 microns and a length of several millimeters. The induced IR-frequency currents excite the lowest order surface waves (Sommerfeld waves), which can propagate over a length of a few millimeters without appreciable attenuation. (This is perhaps the first observation of the use of a wire antenna at a wavelength as short as 10μ .) This antenna is used as the "cat whisker" in a special type of point-contact metal-metal oxide-metal diode as follows: The tip of the thin wire antenna is pointed to a dimension of the order of several hundred Å by means of an etching technique similar to that commonly employed in the production of electron emitting tips in electron microscopy. The cat whisker is then mechanically contacted to a metallic base of copper, nickel, or another metal. Several

pieces of evidence indicate that the oxide layers naturally existing on the metallic base (and/or on the tungsten tip) are maintained in our contact. The diodes are mounted in special housings which permit IR (or far IR) radiation to be coupled to the thin wire antenna in several ways.

When the 10.6μ radiation obtained from the output of a CO_2 laser is coupled to such a diode a rectified DC voltage develops across it. The speed of the diode at 10.6μ is tested by frequency-mixing two simultaneously oscillating 10.6μ P-branch transitions. The mixing signals at the difference frequencies of the various transitions are observed by simultaneously coupling the output of a tunable 54GHz klystron to the diode; a strong zero beat is observed whenever the klystron frequency or one of its harmonics becomes equal to the difference frequency between a pair of simultaneously oscillating P-branch transitions. We are able to observe beat signals between simultaneous oscillations as far apart as 160.5GHz. This corresponds to the mixing of the third harmonic of the klystron frequency at 53.5GHz and the frequencies of P(16) and P(22) CO_2 laser transitions. This experiment has enabled a precise determination of the frequency spacings of various CO_2 P-branch transitions with an accuracy which surpasses previous spectroscopic determinations by a considerable margin.

It must be noted that observation of a DC voltage developed across the diode structure when subjected to a 10.6μ laser radiation is not an indication of a rectification process--such a voltage may also develop as a result of a thermo-electric effect--an effect which is usually slow and not suitable for frequency mixing experiments at very high frequencies. Accordingly, the diodes are tested in several ways through those processes which require high speed of response such as frequency mixing at integer multiples of 54KM/c sec or experiments described below.

In another experimental test of the speed and response of these diodes the frequencies of two different HCN lasers, one operating at 337μ and the other at 311μ , are mixed with the output of a 70GHz (V-band) klystron. In this case the zero-beat signal developed across the diode is so strong that it can be displayed directly on a wideband oscilloscope, without the use of additional electronics to achieve narrowbanding. We are also to obtain a large frequency mixing signal between the 13th harmonic of a V-band klystron and the 337μ HCN laser transition; in this case the diode is simultaneously subjected to the 337μ laser radiation and the microwave radiation of the klystron.

Considerable progress is made toward construction and realization of a frequency multiplier chain to eventually compare infrared laser frequencies in the 10μ range with a microwave frequency and in turn with microwave

of most rotational lines are completely resolved and identified. Wavelength measurements have been done to relative accuracy of one part in 10^7 . Additional radiative effects are analyzed theoretically. These relate to the non-linear effects arising from traveling wave amplification of a broad band radiation field including saturation effects.

The effect of motional narrowing (the decrease in the normal Doppler linewidth when the mean free path becomes comparable to the wavelength of the emitted radiation) in spontaneous Raman scattering in the Q(1) line of the 1-0 vibrational band of the hydrogen molecule is observed and studied in detail. An argon ion laser is used as the exciting source, and the linewidth analysis is done with a Fabry-Perot interferometer. The results show that a theory based on the hard collision model gives a better fit than the diffusion theory.

Theses:

J. H Parks, "A High Resolution Study of Stimulated Ultraviolet Transitions in Molecular Nitrogen: $C^3\Pi_u - B^3\Pi_g(0,0)$ 3370 Å," Ph.D. Thesis, Department of Physics, September, 1968.

Publications:

- L. O. Hocker and A. Javan, "Laser Harmonic Frequency Mixing of Two Different Far IR Laser Lines up to 118μ ", Phys. Letters 26A, 6, pp. 255-256 (1968).
- L. O. Hocker and A. Javan, "Absolute Frequency Measurements of New CW DCN Submillimeter Laser Lines", Appl. Phys. Letters 12, 4, pp. 124-125 (1968).
- M. S. Feld and A. Javan, "Frequency Spectrum of Spontaneous and Stimulated Line Narrowing Effects Induced by Laser Radiation", Phys. Rev. Letters 20, 12 (1968).
- D. Ramachandra Rao, L. O. Hocker, A. Javan and N. Knable, "Spectroscopic Studies of 4.3μ Transient Laser Oscillation in CO_2 ", J. Molecular Spectroscopy 25, 3, pp. 410-411 (1968).
- M. A. Kovacs, D. Ramachandra Rao and A. Javan, "Study of Diffusion and Wall Deexcitation Probability of 00^0_1 State in CO_2 ", J. of Chem. Phys. 48, 7, p. 3339 (1968).
- L. O. Hocker, D. R. Sokoloff, V. Daneu, A. Szoke and A. Javan, "Frequency Mixing in the Infrared and Far Infrared Using a Metal to Metal Point Contact Diode", Appl. Phys. Letters 12, 12, 401 (1968).

frequency standards. This is being done with a "multiplier chain using a laser link". In this chain, a high harmonics of one laser frequency is mixed with a fundamental frequency of another laser and an intermediate frequency in the microwave region. All the frequency mixings are done in the diodes described above. Such a multiplier chain is successfully realized up to 100μ . Experiments are in preparation for further multiplication to shorter wavelengths range.

A new C.W. far infrared laser is constructed which oscillates at 95μ and 211μ (the $3'D \rightarrow 3'P$ and $4'D \rightarrow 4'P$ transitions respectively). This laser is planned for its use as important laser links in the above multiplier chain. Experiments are also in progress to determine with high precision the absolute frequencies of there He laser resonances--measurements of considerable importance to test radiative correction and relativistic effects in He.

A long arm Michelson interferometer is utilized to compare with high precision the wavelength of a visible laser with that of a far infrared laser wave length of known absolute frequency. This is done through a simultaneous fringe counting as the long arm of the interferometer is continuously varied. The interferometer utilizes a large corner reflector. (This experiment is being done in collaboration with F. Zernike, Perkin-Elmer Corp.) An accuracy of one part in 10^6 in wavelength comparison is already achieved. Experiments are in progress to utilize directly a computer in analyzing the data obtained from the interferometer and to allow corrections for fringe shifts due to diffraction. Considerable improvements in accuracy are expected.

An experiment is also underway to compare a $6328 \text{ \AA}$ laser wavelength (stabilized on Lamb dip) with a Kr wavelength standard. This is being done with a scanning Fabry-Perot; a wavelength comparison with an accuracy of 5 parts in 10^9 has already been obtained.

One of the aims of the above series of experiments is to eventually obtain a high precision value of the speed of light constant; also another important future aim is to obtain an ultimate connection between time and length standards.

6.0 Other Gas Laser Experiments

The exceptionally high optical gain of the $C^3\Pi \rightarrow B^3\Pi_g$ ultraviolet ($3600 \text{ \AA}$) band in N_2 produces significant traveling wave narrowing of the Doppler linewidth. This effect is utilized, for the first time, to obtain high resolution spectroscopic information. The fine structure due to Λ -doubling

- P. R. Schroeder, M. S. Dresselhaus, and A. Javan, "Location of Electron and Hole Carriers in Graphite from Laser Magnetoreflexion Data", Phys. Rev. Letters 20, 23, 1292 (1968).
- C. K. Rhodes, M. J. Kelly and A. Javan, "Collision Relaxation of the 10^0_0 State in Pure CO_2 ", J. of Chem. Phys 48, 12, pp. 5730 (1968).
- J. H. Parks, D. Ramachandra Rao and A. Javan, "A High Resolution Study of the $\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g(0,0)$ Stimulated Transitions in N_2 ", Appl. Phys. Letters.
- C. K. Rhodes, A. Szoke and A. Javan, "The Influence of Level Degeneracy on the Self-Induced Transparency Effect", Phys. Rev. Letters 21, pp. 1151 (1968).
- J. Murray and A. Javan, "Motional Narrowing in Hydrogen Raman Scattering", submitted for publication, J. of Mol. Spectroscopy.
- M. S. Feld, A. Javan and P. Lee, "Strong Mode Coupling Induced in a Gas Laser by an Intra-cavity Saturable Absorbing Medium", submitted for publication, Appl. Phys. Letters.
- M. S. Feld and A. Javan, "Laser-Induced Line Narrowing Effects in Coupled Doppler-broadened Transitions", submitted for publication, Physical Review.
- J. S. Levine, P. A. Bonczyk and A. Javan, "Observation of Hyperfine Level Crossing in Stimulated Emission", submitted for publication, Physical Review Letters.

ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES OF
MATERIALS AND DEVICE APPLICATIONS

I. SOLID STATE STUDY GROUP

Faculty:

G. W. Pratt, Jr., Professor, Electrical Engineering
Mildred S. Dresselhaus, Professor, Electrical Engineering
D. Adler, Assistant Professor, Electrical Engineering
D. D. Buss, Assistant Professor, Electrical Engineering
L. G. Ferreira, Research Affiliate, Electrical Engineering

Graduate Students:

L. Johnson, Graduate Student, Electrical Engineering
E. K. Li, Graduate Student, Electrical Engineering
P. G. McMullin, Research Assistant, Electrical Engineering
F. P. Missell, Research Assistant, Physics
N. J. Parada, Research Assistant, Electrical Engineering
C. L. Rieck, Research Assistant, Physics
C. G. Whitney, Graduate Assistant, Physics
H. P. H. Yuen, Research Assistant, Electrical Engineering

Support Staff:

Susan M. Johnson, Secretary, Electrical Engineering

Personnel who have left:

D. D. Buss, Teaching Assistant, Electrical Engineering (Now Assistant Professor at MIT)
L. G. Caron, Research Assistant, Electrical Engineering (Now at Universite de Sherbrooke, Canada)
J. Cheng, Whitney Fellowship, Electrical Engineering (Now at Harvard University)
M. S. Maltz, Research Assistant, Electrical Engineering (Now Xerox Research Laboratory)
P. R. Schroeder, Research Assistant, Physics (Now at Bell Telephone Laboratories, Allentown, Pennsylvania)
P. W. Staecher, Research Assistant, Electrical Engineering (Now at Brooklyn Polytechnic Institute)

Degrees Granted:

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

Sponsorship:

Office of Naval Research, Nonr-1841(72); NRO18-106, DSR 78721
 Army Research Office-Durham, DA31-124-ARO/D/92, DSR 79489
 Advanced Research Projects Agency, SD-90, DSR 75114, DSR 75117
 U. S. Air Force, Lincoln Laboratories Account 11195

Research Report

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

We have successfully caused optically pumped PbSe to lase while subjected to a strain that splits the multi-valley degeneracy in the conduction and valence bands. Under such a strain the material has two separate energy gaps lying at different points of momentum space. There is a separate inverted population associated with each gap, and the optically pumped material behaves like two independent lasers emitting two separate frequencies. At a modest increase in the strain already applied we hope to see stimulated phonon emission when the strain split valleys satisfy energy-momentum conditions. This multiple frequency laser has device applications in that one of the emitted frequencies can be modulated while the other unmodulated frequency is transmitted as a local oscillator. Furthermore, it may be possible to rapidly switch the laser back and forth between the multiple frequencies. We are also investigating the use of this system as a tunable infrared source.

The frequency modulation of a GaAs laser by ultrasonic waves at 1 kmc is being instrumented.

A major theoretical investigation of vacancy states in PbTe has just been completed. Starting from an A.P.W. energy band calculation at $k = 0$, the band structure was accurately determined throughout the entire Brillouin zone by the $k \cdot p$ scheme. The perturbing potential due to a Pb vacancy and due to a Te vacancy were set up and their perturbing effect on

the band structure determined. The Koster-Slater Green's function technique was used taking 1000 points in 1/48th of the zone. It was found that a Pb vacancy drives a state out of the valence band complex, across the energy gap, and into the conduction band. No localized state in the gap appears. Each Pb vacancy removes 4 electrons from the valence band which now has 2 less energy levels. Therefore, each Pb vacancy contributes 2 holes, and no localized state to which these holes can freeze out at 0°K. A similar analysis for a Te vacancy leads to 2 electrons appearing in the conduction band, no levels in the energy gap, and no carrier freeze out at 0°K. We are now attempting to relate the energy of a Pb and Te vacancy to the metallurgical phase diagram.

2.0 Correlation in Narrow Bands-Ferromagnetism-Magnetoelectrics (ONR)

An investigation of a new approach to describing a narrow-band ferromagnet is being studied. The basis of this is the use of one electron orbitals whose nature can be continuously varied between Wannier functions highly localized at separate lattice sites and Bloch functions where the electrons are spread over the entire lattice. The degree of localization is determined variationally. These new one electron functions should be useful in understanding recent photo-emission work that indicates that one-electron momentum conservation breaks down in many situations especially narrow band materials.

A study is being made of the optical properties of magneto electric materials. Of particular interest is the fact that an applied electric or magnetic field can markedly alter the index of refraction and that the index has very different directional properties.

3.0 Magneto-Optical Study of Solids (Air Force, ARPA)

Magnetoreflexion resonances observed in arsenic have been identified with interband Landau level transitions at two different points in the Brillouin zone. Analysis of the symmetry properties of the resonances identified with interband transitions across the band gap of 0.365eV indicate changes in the band ordering of the Lin-Falicov calculated energy band structure in the neighborhood of the T point. The analysis of the second series of interband transitions indicates that they occur about a Q point which has much lower symmetry in the Brillouin zone. In this work, it has been demonstrated that it is possible to interpret magneto-

reflection data at low symmetry points so as to provide the same type of information as is available at high symmetry points - i.e. energy band gaps, band curvatures, non-parabolic effects, symmetry properties, lineshape.

High resolution magnetoreflexion studies in graphite with circularly polarized laser radiation are in progress. These studies have shown that the Landau level separation in the conduction band exceeds that in the balance band in the neighborhood of the K point in the Brillouin zone with the magnetic field along the C axis. When combined with deHaas-vanAlphen data, these results imply the existence of electrons at point K which is contrary to the carrier sign assignment that had been previously made. This carrier sign identification also explains the cyclotron resonance results of Galt et al. which have been in the literature for over a decade.

Interference magnetoreflexion effects have been observed in InSb and are characterized by resonances which are periodic in H rather than in $1/H$ which characterized interband Landau level transitions or optical deHaas-Shubnikov effects. The dependence of the interference magnetoreflexion effect on photon energy, temperature and crystal orientation has been studied. The experimental data have been explained in terms of a magnetic field dependent dielectric constant which becomes prominent in the vicinity of an interband transition.

4.0 Magneto-Optical Studies of Solids

4.1 Band Structure of Magnetic Semiconductors (ARPA)

Magnetic semiconductors, such as transition-metal and rare-earth compounds, are generally characterized by a primarily localized optical spectrum, but a band-like conductivity. In order to use a band structure diagram to interpret both electrical and optical properties of these materials, it is necessary to find a method for representing the highly correlated, localized states in an effective single-particle approach. Such a method has been developed, based on the Hubbard Hamiltonian, which introduces correlations between electrons on the same atom into an ordinary band approach. This Hamiltonian is exact in both the band and atomic limits. There is much experimental evidence that the outer s and p bands of magnetic semiconductors are near the band limit, while the occupied d or f bands are very near the atomic limit. Thus this approximation is expected to be generally applicable to these materials. Because many-electron states must be represented in a single-particle diagram,

some additional rules must be introduced in order to interpret the diagram correctly. It is essential to allow the position of the states to depend on the occupation numbers, and this can be done in a straightforward manner. Furthermore, it is necessary to distinguish between ordinary conducting states (band-like states) and primarily non-conducting states (in which conduction can take place only by means of thermally-activated hopping of small polarons), and this can also be accomplished in a simple way.

4.2 Electrical and Optical Properties of Transition-Metal Oxides (ARPA)

A systematic review of the experimental data on transition-metal oxides has been written, and it has become possible to reach some definite conclusions which were not previously evident. All previous models for these materials assumed that the semiconduction which exists must take place in the cation d band. However, the d band cannot be taken to be an ordinary band, for this leads to the erroneous conclusion that most of the insulating oxides should be metallic. This has resulted in the assumption that the conductivity takes place by means of a thermally-activated hopping process, a model which is in conflict with the transport data, which clearly indicate a band-like semiconduction. An entirely new model has been developed for conduction in these materials. It is postulated that the d electrons are very near the atomic limit and are more properly treated as core electrons than as valence electrons. Thus the d bandwidth is extremely small, as is the d-electron-phonon coupling. Holes in the d band form very small polarons, which can conduct only by means of thermally-activated hopping. However, the hopping time is so long that this conductivity is extremely small. But these holes can also act as acceptors to the oxygen 2p electrons, which form a normal 2p band. At temperatures over approximately 100°K, conduction in the 2p band dominates the thermally-activated hopping of d electrons. At very low temperatures, the small polaron hopping becomes larger than the 2p-band conduction, but it is likely that both are dominated by the impurity conduction resulting from the partial compensation of acceptors by donors. Thus the small-polaron hopping is observable only in ac experiments. This model is in agreement with all the available electrical transport and optical data on NiO, the most thoroughly investigated material, and it is likely that it can be extended to most of the other purely insulating oxides.

4.3 Metal-Nonmetal Transitions (ARPA)

Transition-metal oxides and sulfides can be broken down into three groups - insulators, metals, and materials which undergo insulator-metal transitions as the temperature is raised. A surprising feature is that the populations of all three classes is roughly the same. The recently developed model which attributes most of the metal-nonmetal transitions to an extra energy gap arising from the lowering of symmetry brought about by a crystalline distortion, antiferromagnetic ordering or a combination of the two, provides a simple explanation of this apparent puzzle. These materials can be classified by width of the d band: those which have wide d bands (e. g. TiO , CrO_2) are metallic; those which have very narrow d bands (e. g. NiO , MnS) are Mott insulators; those which have intermediate d bands (e. g. VO , NiS) could support metallic conductivity, but at low temperatures reduce their free energy by distorting, ordering antiferromagnetically, or both and become insulators. In the third group, the necessary decrease of band gap with thermal excitation of carriers, taken together with the greater electronic contribution to entropy in the metallic state, result in a first-order nonmetal-metal transition at a critical temperature. A detailed study of the experimental data obtained thus far leads to the following tentative conclusions. The transitions in VO_2 , NbO_2 , Ti_3O_5 , V_3O_5 , V_4O_7 , Mo_9O_{26} , CrS , and tetragonal FeS are due to crystalline distortions. The transitions in NiS and Ti_5O_9 arise from antiferromagnetic ordering. The transitions in V_2O_3 , VO , V_6O_{13} , and hexagonal FeS result from a combination of crystalline distortion and antiferromagnetism. Only Ti_2O_3 , which appears to be an example of simple band overlap, and Fe_3O_4 , which possibly exhibits a Mott transition, do not seem to fall into one of these three groups.

4.4 Narrow Energy Band Theory (ARPA)

Some rigorous results regarding the atomic limit of narrow energy band theory have been obtained. In particular, it has been shown that even for zero bandwidth, the single-particle Green's function of the Hubbard Hamiltonian is non-diagonal in the Wannier representation where there is a non-integral number of electrons per atom, and thus current-carrying states exist in this limit. A simple method, based on the results of the atomic limit calculation, has been suggested for improving Hubbard's first approximation. This leads to a lower total ground state energy than was obtained by Hubbard, and also appears to give a more accurate result

for the magnetic properties of the ground state, at least in the limit of large intraatomic Coulomb repulsion.

Theses:

- D. D. Buss, "Characterization of the Lattice Vibration Spectrum in PbTe," Ph. D., Department of Electrical Engineering, August 1968.
- M. S. Maltz, "A Magnetoreflexion Study of Arsenic and Bismuth," Ph. D., Department of Electrical Engineering, June 1968.
- P. W. Staecher, "High Resolution Magneto-Reflection of InSb," E.E., Department of Electrical Engineering, September 1968.

Publications:

- G. W. Pratt, Jr., and L. G. Caron, "Correlation and Magnetic Effects in Narrow Energy Bands I," J. Appl. Phys. 39, 485 (1968).
- L. G. Caron and G. W. Pratt, Jr., "Correlation and Magnetic Effects in Narrow Energy Bands II", Rev. Mod. Phys. (in press).
- P. R. Schroeder, M. S. Dresselhaus, and A. Javan, "Location of Electron and Hole Carriers in Graphite from Laser Magnetoreflexion Data," Phys. Rev. Lett. 20, 1292 (1968).
- S. Rabbii, "Investigation of Energy-Band Structures and Electronic Properties of PbS and PbSe," Phys. Rev. 167, 801 (1968).
- M. Maltz and M. S. Dresselhaus, "Observation of Interband Transitions in Arsenic," Phys. Rev. Lett. 20, 919 (1968).
- P. T. Bailey, "Knight Shift in Lead Telluride via Relativistic Augmented-Plane Wave Functions," Phys. Rev. 170, 723 (1968).
- D. Adler, "Properties of Transition Metals and Alloys," in Magnetism and Magnetic Materials Digest, W. D. Doyle and A. B. Harris, eds., Academic Press, N. Y., pp. 50-73 (1968).
- D. Adler and R. V. Lange, "The Zero Bandwidth Limit of the Hubbard Hamiltonian," Bull. Am. Phys. Soc. 13, 412 (1968).
- D. Adler, "Insulating and Metallic States in Transition-Metal Oxides," in Solid State Physics, 21, F. Seitz, D. Turnbull, and H. Ehrenreich, eds., Academic Press, N. Y., pp. 1-113 (1968).
- J. Feinleib and D. Adler, "Band Structure and Electrical Conductivity of NiO," Phys. Rev. Letters 21, 1010 (1968).
- D. Adler, "Mechanisms for Metal-Nonmetal Transitions in Transition-Metal Oxides and Sulfides," Rev. Mod. Phys. 40, 714 (1968).
- D. Adler, "Phase Transformations in Transition-Metal Oxides," Science 159, 1133 (1968).
- D. Adler and H. Brooks, "Electrical Properties of Transition-Metal Compounds," Comments on Solid State Physics 1, 145 (1968).
- D. Adler and J. Feinleib, "Band Structure of Magnetic Semiconductors," J. Appl. Phys. (to be published).

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 Superconductivity in Ultra-High Magnetic Fields

We have completed a study of the effect of magnetic impurities on the properties of very high field materials, where Pauli paramagnetism plays an important role in limiting the upper critical field of superconductors.

When there is an antiferromagnetic exchange interaction between the conduction electrons and the localized impurity spins, we find that a novel form of high-field superconductivity can result. When the external field is sufficiently large, it can cancel the exchange field due to the aligned magnetic impurities. Superconductivity in megagauss fields may thus be possible with the utilization of magnetic impurities.

We have also studied qualitatively the effects of a) the magnetic field on the orbital motion of the electrons; b) non-diagonal components of the electron-magnetic impurity scattering, and c) spin-orbit scattering. These effects are detrimental to the high-field superconducting state, and we have shown that under certain conditions these effects can be minimized.

2.0 The Width of the Superconducting Transition

When the temperature is raised above the superconducting transition temperature, the resistance of a metal increases to its normal value. Although the transition can be quite sharp in homogeneous bulk samples, it is significantly broader in thin films.

With the aid of thermodynamic fluctuation theory and the time-dependent Ginzburg-Landau equation, we are developing a theory of the width and shape of the resistive transition of a Type-II superconductor in the mixed state. Preliminary results show that the transition is considerably

broader than in the absence of a magnetic field.

A useful application of this work is to the problem of noise in superconducting bolometers. Recent experiments¹ have shown that the noise can be significantly reduced by the application of a very small magnetic field. We intend to study the effect of magnetic fields on the spectrum of voltage fluctuations, in order to gain a better understanding of this rather remarkable phenomenon.

3.0 Superconductivity in One and Two Dimensional Systems

Little² has proposed that it may be possible to synthesize an organic molecule which will be superconducting at room temperature. However, it has been argued³ that thermal fluctuations would prevent superconductivity from occurring in what would be an essentially one-dimensional system. In fact it has been proved rigorously⁴ that superconductivity is not possible in infinite one and two-dimensional systems. In reply, Little⁵ has argued that an electronic state with a minutely small resistivity is nonetheless possible in a one-dimensional system of finite size.

In order to investigate this hypothesis, we are studying the effect of the collective modes on the range of superconducting correlations in one and two-dimensional superconductors. Our method relies on the use of the time-dependent self-consistent field approximation to obtain the response of the superconductor to a time- and space-varying electromagnetic field. From the response functions, we will obtain the two-particle density matrix so that we can learn the effect of the collective modes on off-diagonal long range order.

References:

1. M. Maul, Ph.D. Thesis, Department of Electrical Engineering, MIT
2. W. A. Little, Phys. Rev. 134A, 1416 (1964).
3. R. A. Ferrell, Phys. Rev. Letters 13, 330 (1964).
4. P. C. Hohenberg, Phys. Rev. 158, 383 (1967).
5. W. A. Little, Phys. Rev. 156, 396 (1967).

Publications:

- L. W. Gruenberg, "Impurity Scattering in Superconductors," Phys. Rev. 170, 491 (1968).
- L. W. Gruenberg and L. Gunther, "Effect of Orbital Quantization on the Upper Critical Field of Type-II Superconductors," to be published in Physical Review 175.
- B. B. Schwartz and L. W. Gruenberg, "Ultra-high Critical Field in Superconductors with Magnetic Impurities," to be published in Physical Review.

III. SEMICONDUCTOR MATERIALS AND DEVICES

Faculty:

R. B. Adler, Professor, Electrical Engineering
P. E. Gray, Professor, Electrical Engineering
R. H. Rediker, Professor, Electrical Engineering
L. L. Chang, Associate Professor, Electrical Engineering
A. C. Smith, Associate Professor, Electrical Engineering
R. D. Thornton, 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. Berninger, Instructor and Graduate Student, Electrical Engineering

Research Staff:

Dr. F. Ruedenauer, Research Associate, Electrical Engineering
R. White, DSR Staff, Electrical Engineering

Graduate Students:

M. Adler, Research Assistant, Electrical Engineering
J. Borky, Research Assistant, Electrical Engineering
R. Broderson, NSF Fellow, Electrical Engineering
S. Brown, NSF Fellow, Electrical Engineering
R. J. Finke, NSF Fellow, Electrical Engineering
D. Fisher, Special Student, Electrical Engineering
C. G. Fonstad, Jr., NSF Fellow, Electrical Engineering
W. Gajda, Teaching Assistant, 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. Mathur, Research Assistant, Electrical Engineering
J. Lowney, Research Assistant, Electrical Engineering
S. Marshall, Research Assistant, Electrical Engineering
E. Pahl, Research Assistant, Electrical Engineering

SECTION B - ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES 83

R. Refowitz, NSF Fellow, Electrical Engineering
D. Reinhard, Graduate Student, Electrical Engineering
R. Siegel, Research Assistant, Electrical Engineering
R. Solomon, NSF Fellow, Electrical Engineering
S. M. Spitzer, NASA Fellow, Electrical Engineering
H. St. Onge, Research Assistant, Electrical Engineering
R. Van Brunt, Undergraduate Student, Electrical Engineering
J. Womac, Research Assistant, Electrical Engineering

Support Staff:

C. R. Grant, Engineering Assistant, Electrical Engineering
Dorothy Chapman, Technician, Electrical Engineering
R. Kelley, Technician, Electrical Engineering
W. Pitkin, Technician, Electrical Engineering
D. Saar, Student Technician, Electrical Engineering
G. Shawnessy, Instrument Maker, Electrical Engineering
Berylee Schutz, Secretary (part time) Electrical Engineering
Jarmila Z. Hrbek, Secretary (part time), Electrical Engineering

Personnel who have left:

D. H. Navon, Associate Professor (Visiting) (to University of Mass.)
J. N. Churchill, Assistant Professor (to University of California, Davis)
J. H. Serebrinsky (to Atomic Energy Commission, Buenos Aires, Argen.)
L. Castro, (to NSA, Washington)
D. Chanoux, (graduated)
D. Evans (to ESL, M.I. T.)
R. H. Greischar (graduated)
V. S. Iyer (graduated)
H. Jenssen (to Crystal Physics Lab., M.I. T.)
T. K. Kaplan (graduated)
J. Kassakian (to Power System Group, M.I. T.)
R. E. Lee (to Bell Telephone Laboratories)
P. C. Lindsey, Jr. (to Texas Instruments, Dallas, Texas)
J. R. Lowney (to Naval Ordnance Laboratory)
W. H. Matthews (to Political Science Department, M.I. T.)
T. Schlax, (to General Motors)
M. Perella (to Nuclear Metals, Concord, Massachusetts)

Degrees Granted:

R. Broderson, S. M. and E. E., Electrical Engineering, June 1968
 L. Castro, S. M., Electrical Engineering, June 1968
 D. Chanoux, S. B., Electrical Engineering, June 1968
 R. J. Finke, S. M., Electrical Engineering, September 1968
 R. Greischar, S. M., Electrical Engineering, February 1968
 T. K. Kaplan, S. M., Electrical Engineering, September 1968
 V. S. Lyer, S. M., Electrical Engineering, June 1968
 R. E. Lee, S. M., Electrical Engineering, June 1968
 P. C. Lindsey, Jr., S. M., Electrical Engineering, June 1968
 J. R. Lowney, S. M., Electrical Engineering, June 1968
 H. P. Jenssen, S. M. and E. E., Electrical Engineering, February 1968
 T. Schlax, Pd. D., Electrical Engineering, June 1968
 R. Solomon, S. M., Electrical Engineering, September 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75112, 75115, 75119
 National Aeronautics and Space Administration NsG 496(part), DSR 76191;
 also Electronics Research Center, NgR 22-009-234, DSR 70574
 Office of Naval Research, Nonr-1841(51), DSR 77984; N000 14-67-A-0204-
 0010, DSR 70421
 U. S. Department of Commerce, Northeast Corridor Transportation
 Project, C-85-65, DSR 76104
 General Motors Corporation Grant
 Air Force Office of Scientific Research, AFOSR-68-1571, DSR 71013
 U. S. Army Electronics Command, DA-28-043-AMC-01978E,
 DSR 76252 (terminated)
 Ford Foundation Fellowship
 NSF Research Initiation Grant, DSR 70393 (terminated)
 NSF Fellowships
 NSF Traineeships
 NASA Fellowship
 M. I. T. Sloan Fund for Basic Research
 High-Voltage Engineering Laboratory Endowment Fund
 M. I. T. Lincoln Laboratory
 NSF Educational Equipment Grant, DSR 11444

Research ReportSurvey

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 Absorption1.1 Two-Photon Franz-Keldysh Effect and Related Non-linear Optical Phenomena

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

Sponsorship: NSF Research Initiation Grant; Advanced Research Projects Agency; Ford Foundation Fellowship

Preliminary theoretical analysis of multiphoton interaction in a semi-conducting material indicates that resulting parametric currents are broadened in frequency content in the presence of a constant electric field. The broadening is similar to that of the photon-induced currents employed in the explanation of the conventional Franz-Keldysh phenomenon, but the effect is quite substantial if one of the two incident light beams is coherent and intense.

1.2 Electro-Absorption in SrTiO_3

Personnel: F. O. Arntz; T. Kaplan

Sponsorship: Advanced Research Projects Agency

Electroabsorption measurements near the optical absorption edge in SrTiO_3 have been performed using polarized light and a configuration with the electric field oriented perpendicular to the direction of light propagation,

but along a cubic axis of the material. In the temperature range 35°K to 100°K, the electroabsorption results reveal a major peak with subsidiary structure on its low energy side. The evidence suggests that the major peak is due to a direct unallowed transition. The subsidiary structure, at present, is not understood. An interpretation of the direct unallowed transition seen in the electroabsorption data in terms of the Kahn and Leyendecker band calculation for SrTiO₃ indicates that at least one of the band extrema lies at a Γ or X point in the cubic Brillouin zone. The electroabsorption results show that the band gap of the material at 100°K is between 3.33 and 3.34 electron volts. An S.M. thesis on this work has been completed by Mr. Kaplan (see Theses).

1.3 Optically Pumped Absorption in II - VI Compounds

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

Sponsorship: Advanced Research Projects Agency

Trapping kinetics are usually studied by techniques which do not permit facile separation of various contributing effects. Experimental apparatus capable of providing more direct determinations of trap occupancy has been constructed. Small changes in the optical transmission of materials, induced by pumping and bleaching radiations, may be measured with this equipment. The alternate bleaching and pumping irradiations modulate the optical transmission of a sample by producing repetitive variations in the occupancy of defect centers inside the material. Preliminary transmission measurements on single-crystal ZnSe in the wavelength range of 0.9 μ m to 2.1 μ m indicate that it is possible to measure a change of optical transmission on the order of fifty parts per million. Thus, the present technique is two to three orders of magnitude more sensitive than conventional optical absorption measurements, when applied to evaluation of low densities of defect centers.

1.4 Temperature-Modulated Optical Absorption in Gallium Arsenide

Personnel: F. O. Arntz; D. K. Reinhard

Sponsorship: Advanced Research Projects Agency

Temperature modulation of optical absorption near the fundamental

electronic absorption edge in p-type GaAs has been investigated using synchronous detection techniques. The modulation was measured at temperatures of 20°K, 80°K, and 300°K. Theoretical analysis based on Redfield's model*, which relates the shape of the absorption tail to the internal electric fields associated with impurities, was carried out for comparison with the experimental results. We find the magnitude of modulation observed at 300°K is substantially larger than the Redfield model would suggest but obtain agreement at the lower temperatures. Consequently, we conclude that multiphonon effects account for the edge broadening at room temperature and above, but regard Redfield's model as appropriate at lower temperatures. An S. M. thesis on this topic has been completed by Mr. Reinhard (see Theses).

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

2.0 Interaction of Successive Diffusions

2.1 Phosphorous and Boron in Si

Personnel: R. B. Adler; E. Prah, R. J. Finke

Sponsorship: Advanced Research Projects Agency, NSF Fellowship

Mr. Prah has succeeded in reproducing the "retardation" effect originally observed and reported by J. E. Lawrence in p-n-p sequential double diffused structures with high phosphorous concentration in the base. He is trying to determine whether this effect depends upon the cooling rate after the emitter diffusion. Efforts to find "precipitates" in these "retardation" structures are also underway using transmission electron microscopy.

Mr. Finke in his S.M. thesis (see Theses), has looked at the "enhancement" or "dip" effect in p-n-p sequential double-diffused structures in two respects: experimentally, to ascertain any differences between diffusions into the usual {111} planes and those into {100} planes; analytically, to ascertain by numerical machine methods, over what portion of the base region, back from the original collector-base junction, the diffusion coefficient must be enhanced, and by what factor, to account for the observed "dips" on the assumption that the dips develop only during the cooling time of about 10 seconds.

The experimental problem was aimed at exploring rather directly the

model of the n-p-n dip effect which attributes it to vacancies produced by the non-conservative growth of dislocations into the material from its upper emitter region during cooling. Such non-conservative growth is expected to occur in Si in the $\langle 111 \rangle$ directions, but not in the $\langle 100 \rangle$ directions.

Our findings show about a factor of two greater dip for $\langle 111 \rangle$ axis diffusions than $\langle 100 \rangle$ axis diffusions. Specifically, with base surface concentration $2 \times 10^{20} \text{ cm}^{-3}$, emitter surface concentration $5 \times 10^{20} \text{ cm}^{-3}$, and an undisturbed base width of 0.75μ , the dip effects are $0.2 \mu \langle 111 \rangle$ and $0.1 \mu \langle 100 \rangle$.

Moreover, the theoretical study confirms that the enhancement of the diffusion coefficient must occur over a significant portion of the base quite near to the original collector junction, but requires a diffusion coefficient of the order of only 75 times the value of the normal one at the high diffusion temperature, to account for the measured dip (previous work has suggested the need for a factor of about five hundred). Conversely, even a factor of 1000 enhancement of the diffusion coefficient of base impurity throughout the entire emitter region (but no enhancement at all in the base region) fails to account for the observed dip. All these calculations were carried out for several different initial profiles of the base impurities, to determine whether the well-known anomalously fast diffusion of these in their high concentration regions would be important in the present context.

2.2 Arsenic and Gallium in Ge

Personnel: R. B. Adler; B. Mathur

Sponsorship: Advanced Research Projects Agency

We are now able to polish Ge slices and to perform and evaluate acceptable diffusions of As into them. We are engaged in learning the masking methods already available here in another group (see Section 11.0). It is our intention to observe diffusion interactions, first with $n^+ p n$ structures of conventional double-diffused form.

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

3.1 Theory of the Strain and its Electronic Effects

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

Our study, begun last year, of interface strains in the systems silicon-silicon oxide, silicon-silicon nitride, and silicon-silicon oxide-silicon nitride has continued. Silicon crystals have been found to deform inelastically upon pyrolytic deposition of silicon nitride films thicker than about 3 microns; a polygonization process is probably involved. The bending of Si samples turned out to be dependent on the cooling rate after deposition, in particular for samples involving silicon-oxide-nitride. It is not clear whether this is a creep-like process or involves structural changes in the films.

A reevaluation was also made of the elastic bimetallic-type problem involved in the silicon-insulator systems. Numerical solution was undertaken for several configurations in a plane stress approximation, using the EPS program (developed by Coyt Tillman, of MAC Project). Large stress concentrations were found near discontinuities in the film (resembling masking holes), with maximum stresses of nearly 10^9 dynes cm^{-2} (two orders of magnitude larger than those found using Saint Venant approximation). At such stresses changes may be expected in the electronic band structure of the Si, and some experiments were conducted in order to find out whether such changes were actually present. Mr. Serebrinsky found some changes in the infrared (.96 micron) transmittance of Si crystals in the vicinity of the stress concentration region near discontinuities in the insulating films. These changes can be explained in terms of deformation potentials. Mr. Refowitz' efforts to examine electronic effects as functions of position along the Si-Insulator interface by MOS methods ran into essentially technological difficulties, as is described in his S. M. thesis.

3.2 Theory and Application of X-ray Topography

Personnel: R. B. Adler; W. Gajda

Sponsorship: Advanced Research Projects Agency

A study of the X-ray scattering from strained lattices is nearing completion. Several theoretical methods of attack have been tried, but the most successful has been the use of a deformed Darwin model. The crystal is modeled as a series of parallel planes which are perfect with the exceptions of local regions in which the strain field is represented as a deformation in each plane. The scattering of the individual plane is treated as a Fresnel diffraction problem and the response of the entire crystal to an incident wave train is determined by solving a set of

difference equations relating the local transmitted and diffracted beams. This approach yields good agreement with observed experimental results from topographs of Si substrates strained by surface films.

We have also advanced our understanding of the basic topographic contrast mechanism as set forth by Lang, i. e. - the integrated intensity diffracted by an ideally imperfect crystal is about one to two orders of magnitude greater than that diffracted by an ideally perfect crystal. It is often overlooked that the concept of integrated intensity implies a divergent incident beam in the Lang experimental configuration. The ideally imperfect crystal displays a greater diffracted intensity, not because it is a more efficient scatterer for plane waves arriving at angles close to the Bragg angle, but because its angular response is greater than that of the perfect crystal. It does not appear that this point has been sufficiently stressed in the literature, and indeed the common term 'Extinction Contrast' is really a misnomer.

A careful study of the question of topographic resolution has been made in an attempt to reduce exposure times without an attendant loss of resolution. The basic Lang technique, using either a micro-focus or a spot-focus X-ray tube, requires about two hours of exposure for each mm. of crystal scanned. By using a line-focus tube and slit system (different in concept from the method proposed by G. H. Schwuttke), we have been able to reduce the time requirement to 0.75 mm/hour without loss of resolution. The basic concept in this method is to reduce the effective height of the source 'seen' by each point in the crystal being scanned.

Continued topographic investigations of Si substrates strained by SiO_2 and Si_3N_4 films have revealed new, previously unreported, contrast effects which present features of the strain fields at variance with models proposed by other investigators. The details of this work will be published in the near future.

4.0 Thermophotovoltaic Energy Conversion

Personnel: P. E. Gray, B. D. Wedlock; J. G. Kassakian.

Sponsorship: U. S. Army Electronics Command

This work has been terminated, with a final report to the contractor (see Publications). However, some theoretical studies related to this problem are described in Section 5.0 below.

5.0 High Injection Effects in Semiconductors

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

Sponsorship: U. S. Army Electronics Command; Advanced Research
Projects Agency

In Mr. Schlax' doctoral thesis, a careful computer analysis of the transverse voltages developed in the base region of a transistor was carried out (see Theses). A major lesson from that work is the validity, over a wide range of common conditions, of the approximation that the transverse component of the minority-carrier current is negligibly small. Coupled with the normal property that the longitudinal component of majority-carrier current is also negligible, the new point of view lends itself directly to analytical treatment. Such a treatment has been applied by Mr. Castro to planar p-i-n photovoltaic energy converters with all junctions on the dark side. He has found the short-circuit current, collection efficiency, a worst-case series resistance, and other features of the solution in the intrinsic region, for situations in which the two carriers have equal diffusion coefficients (see Theses).

Mr. Lowney's Master's Thesis on transport phenomena at high injection levels has been completed, according to the following abstract:

A p-i-n germanium diode was pulsed with current to establish high injection in the intrinsic region. The technique of infrared absorption by free carriers was used to determine the injection level. Then the diffusion and decay of a perturbation pulse superimposed upon the main pulse were measured with a back-biased rectifying probe contact. From these measurements together with experimentally verified theoretical values for carrier mobilities, the ambipolar diffusion coefficient and incremental lifetime were determined.

The results showed that the incremental lifetime decreased from about 50 μsec to about 5 μsec from an injection level of approximately $2.3 \times 10^{16}/\text{cm}^3$ to one of approximately 2.5×10^{17} per cm^3 . The ambipolar diffusion coefficient decreased from about 50 cm^2/sec to about 30 cm^2/sec over the same range, as predicted by the theory of hole-electron scattering.

It must be pointed out that the measured values of incremental lifetime and ambipolar diffusion coefficient are not related in a simple way to the device behavior at high injection, since the continuity equation becomes

non-linear. However, the data agreed with that predicted by the Einstein relation, which may be used to simplify the continuity equation somewhat.

6.0 Nuclear Magnetic Resonance in Solids

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

Sponsorship: Office of Naval Research, NSF Fellowship

The research programs reported below are a continuation of our work on lead telluride and other lead salts. They are a straightforward extension of our experimental techniques to a class of ferroelectric mixed crystals $[\text{Na}_x\text{K}_{1-x}\text{TaO}_3]$ of great interest to several other groups here concerned with problems of long-range order in ferromagnetic and related (ferroelectric) systems. We seek, using nuclear magnetic resonance and other techniques, to extend the fundamental understanding of the electronic structure and electrical properties of these materials.

6.1 Knight Shift in Lead Telluride

We have continued to accumulate data on the temperature and carrier concentration dependence of the Pb^{207} Knight shift in p-type lead telluride between 55°K and 470°K. The earlier measurements were made in cooperation with Drs. Hofman and Sagalyn of the Army Materials and Mechanics Research Center, while more recent measurements have been carried out in our own laboratory.

The data continue to support our general theory based on the changing carrier degeneracy with temperature and on the occupation of a second valence band at high temperatures. But quantitative analysis of these data depends in a critical way on the specific energy level model one chooses for the lead telluride valence band. The existing models all show internal inconsistencies, which limit the credence one can give to the analysis of any experiment, whether of transport, Knight shift or optical properties. Accordingly, a comprehensive review of the available literature has been carried out, and the available experimental data of all types are being correlated with the theoretical calculations of Professor Pratt's Materials Theory Group in an attempt to develop an improved energy band model for the lead telluride valence band.

On the experimental side, the weak NMR signals in lead telluride can now be observed routinely (See Section 6.4 below.) A temperature control system for varying the NMR sample temperature has been designed. We are continuing our program of annealing of lead telluride samples to control

the carrier concentration.

6.2 Knight Shift in (PbSn) Te and (PbSn)Se Alloys

This experiment is a natural outgrowth of the lead telluride work. The valence and conduction bands of both alloy systems (lead tin selenide and lead tin telluride) are postulated to cross at particular proportions of lead and tin. We are attempting to investigate this band crossing with NMR studies of the Knight shift in these materials. Several lead-tin selenide samples have been obtained, and preliminary Pb²⁰⁷ Knight shift measurements have been made. Selected Hall effect measurements and the broad NMR line observed suggest that the samples must be annealed in a controlled atmosphere to improve sample uniformity.

6.3 NMR in Ferroelectric Na_xK_{1-x}TaO₃

A cryostat for working in the solid nitrogen range (55°K) has been assembled, and preliminary measurements have now been made on the Na²³ resonance in Na_{0.48}K_{0.52}TaO₃. We have also observed the Ta¹⁸¹ resonance in KTaO₃ and the Nb resonance in K Nb_{0.2}Ta_{0.8}O₃. We have not yet observed these in the ferroelectric phase and this will be the next step in this project.

6.4 NMR Instrumentation

As referred to in Section 6.1 above, Mr. Hewes, drawing on the theoretical and experimental work in Mr. M. Adler's Master's Thesis, has designed a nuvistORIZED NMR autodyne spectrometer with outstanding signal-to-noise characteristics. This spectrometer has been adapted for use in all three major experiments. Further investigations of its sensitivity and performance are being carried on.

7.0 Microelectronics

7.1 Field Effect Transistors

Personnel: B. D. Wedlock, R. B. Adler

Sponsorship: Advanced Research Projects Agency

A theoretical study of the phenomenon of "pinch-off" in a junction field-effect transistor has been carried out by Professor Wedlock. The results have provided a new physical picture of the operation of this device in the current saturation region. Based on this new physical picture, a one-dimensional model approximation has been formulated. The volt-ampere characteristics calculated from the model are in close agreement with experimental data for values of drain-to-source voltage both above and below pinch-off. A second feature of the model is that it predicts a finite incremental output resistance varying with geometry in accordance with the experimentally observed behavior.

7.2 Thin Film Devices

Personnel: D. Navon, D. L. Smythe; R. H. Greishar

Sponsorship: NASA Electronics Research Center

Mr. Greishar's S.M. Thesis summary concerning the completed work on GaAs films, is as follows:

Thin evaporated films of gallium arsenide were grown from the elements on amorphous glass substrates. These films were very hard and showed good adhesion to the substrates. Electrical measurements of conductance in the plane of the film were made by means of electrodes evaporated in parallel strips on top of the films.

Conduction normal to the plane of the film was measured using overlapping evaporated electrodes, one under the film one on top of it. Conduction in this direction was linear for applied voltages less than about 100mv. For voltages larger than this, a power relation of the form:

$$I = KV^{T_c}/T + 1$$

where K and T_c are constants, gave a good fit to the observed voltages V and currents I. A V-I characteristic of this form, namely, a linear variation of current with voltage for small voltages and of the above form for higher voltages, can be explained by space charge limited current flow controlled by an energy distribution of traps of the form

$$N_t(E) = A \exp(E/k \cdot T_c)$$

where N_t is the density of traps at energy E, and A and T_c are constants.

The apparent magnitude of the conductivity, calculated using the conductance obtained from the linear portion of the V-I characteristic suggested poor electrode contact to the film; namely, only about 1 percent of the total area of electrode overlap was conducting.

7.3 Integrated Circuits

Personnel: R. B. Adler; R. L. Solomon

Sponsorship: Advanced Research Projects Agency; NSF Fellowship

Mr. Solomon considered limitations on the packing density of integrated circuits with the following S.M. Thesis abstract:

Ultimate miniaturization of high speed sequential logic circuits is restricted by high frequency and thermal interactions which result from the fast speeds and the necessary relatively large power levels of present day circuits. This thesis seeks to uncover more fundamental limitations of packing density. Macroscopic thermal and displacement current interactions are minimized by choosing power levels and frequencies which are several orders of magnitude lower than those encountered in present logic circuits. The question to be answered is whether or not relatively low speed, high density systems are more efficient than high speed circuits packed at relatively lower densities. The measure of efficiency is taken to be the number of logic functions performed per unit volume per unit time by the system.

The system considered here consists of cubic geometry logic circuits stacked in a three dimensional array with silicon as the host lattice. The first part of the analysis determines the microscopic limitations on the size of the bulk regions of individual devices due to the statistical variation of doping atoms. The allowable spacing of devices is then investigated using the minimum device sized calculated earlier. Parasitic interactions such as noise, thermal effects and stray coupling currents yield a minimum size for the overall system.

Nanowatt circuits are developed which use non-linear diode characteristics to achieve the necessary high impedance levels. A system with one billion devices per cubic centimeter operating at 100KHz is shown to obey interaction constraints which were earlier derived and is thus theoretically feasible.

8.0 Electric Propulsion

Personnel: R. D. Thornton; S. Brown, S. Marshall, R. VanBrunt,
D. Saar

Sponsorship: U. S. Department of Transportation; General Motors Corp.

Mr. Brown and Mr. Saar continued the development of solid state switching circuitry for driving our experimental motor (previously constructed by Mr. C. Erdelyi). The motor was run successfully at currents over 100 amps and it is expected to operate at about 25kw output. Speed control circuitry was developed by Mr. Van Brunt to drive the motor from a constant DC supply. The motor and controls have been tested both in the laboratory and, at reduced power levels, in the MIT Experimental Electric Car. New wheel motors are being built and will utilize the same electronics but achieve higher power output and efficiency. Mr. Marshall continued the development of a linear synchronous motor which appears to have promise for dual mode transportation system and possibly for a high speed train.

9.0 High Power Solid State Devices

Personnel: D. Navon, R. D. Thornton; J. Serebrinsky; E. A. Miller,
P. C. Lindsey, J. M. Borky, D. Fisher

Sponsorship: National Aeronautics and Space Administration; U. S.
Department of Transportation

Mr. Borky initiated design and fabrication of a power transistor incorporating built-in negative thermal feedback to compensate for the inherent positive thermal feedback which causes thermal instabilities such as second breakdown. By making a power transistor as an array of lower-power transistors, and by using a separate and thermally coupled driver stage for each power transistor in the array, it is expected that a higher power and more failure-tolerant design can be achieved. Work is also continuing on modeling the thermal feedback so that computer simulation can be effected. Mr. Serebrinsky has demonstrated some new and possibly better methods of providing high current contacts. Mr. Lindsey has done an extensive analysis of the behavior of carriers in the high resistivity region of a high voltage transistor operating in

saturation. Work by Mr. Fisher has explored methods of increasing the voltage capabilities of a transistor. Professor Navon has extended the analysis of Mr. Miller to explain some of the thermal properties of transistors.

10.0 Study of Basic Device Parameters in the Lead Salts

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

Sponsorship: Office of Naval Research, National Science Foundation
Fellowship

The goal of this program is to study in detail some of the physical parameters related to the performance of devices in PbSe. Better understanding of these parameters and the ability to control them should lead to improvement of lasers and detectors of infrared radiation and to broader applications of these materials, including the mixed lead-tin chalcogenides, to new devices.

We have chosen to work with lead selenide for our initial efforts, feeling that it is representative of the lead salts, both in its physical properties and in its promise for device applications. Programs have been undertaken in three areas: The study of interdiffusion of Pb and Se in PbSe and the properties of diffused p-n junctions produced by this interdiffusion. The study of high-field conduction processes in homogeneous bulk samples of PbSe. Lifetime measurements by the decay of luminescence from optically pumped PbSe over the full available range of concentrations and as a function of temperature.

In the interdiffusion program, the depth of p-n junctions in the lead chalcogenides has been calculated by using different diffusion coefficients for the p and n-type material, $D_p > D_n$ to solve the interdiffusion problem. The solutions to the diffusion equation have been obtained for two cases of one-dimensional geometry: the semi-infinite solid and the slab of finite thickness. The results are useful in predicting the movement of p-n junctions, in determining the equilibration time required for obtaining homogeneous material and in predicting concentration profiles. The movement of p-n junctions and equilibration times are discussed in terms of an effective constant diffusion coefficient D^* and approximate analytical expressions are obtained for it. For p into n diffusion is larger $D^* \geq D_p$ and for n into p diffusion $D^* \leq D_n$ for the semi-infinite case. Experimental

work on diffused p-n junctions has been undertaken and the experimental results agree very well with our theory.

In the study of high-field conduction processes, the equipment has been assembled. A high-voltage pulser operated by a wetted relay has been used to produce current pulses in PbSe samples of up to 80 A amplitude with rise times of the order of 1 nsec and pulse duration of the order of 10 nsec. The sample in series with a 1 ohm coaxial resistor terminates a 50 ohm coaxial line. The current as measured across the 1 ohm resistor and the sample voltage are displayed on a dual-beam sampling oscilloscope. Samples as small as $40 \times 40 \times 150$ (microns)³ are being fabricated in order to reduce the requirements on the pulser voltage and current and to minimize sample heating.

In the study of bulk lifetime, the GaAs laser and the PbSe sample to be investigated are located in a variable temperature, optical dewar in which the temperature can be controlled to 0.1°K . The photoluminescence from the cleaved or etched illuminated surface of the PbSe is collected by a system of mirrors and focussed upon a copper-doped germanium infrared detector which is located in a second liquid helium dewar. An impedance transforming amplifier must be located within the detector dewar in order to minimize the stray capacitance in parallel with the detector, that limits the response time. The amplified pulse is displayed on a sampling oscilloscope. Luminescence from PbSe has been observed on several p-type samples near 4.2°K and on one n-type sample from 4.2°K to 140°K . The lifetimes in these samples were in the range of 0.1 to 1 μsec .

11.0 Photoluminescence from Semiconductors

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

Sponsorship: NASA (MIT Center for Space Research), Advanced Research
Projects Agency, Air Force Office of Scientific Research, Ford
Postdoctoral Fellowship

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

In direct gap semiconductors the field control of luminescence is being studied. Both silicon nitride and SiO_2 have been deposited on GaAs and techniques are being developed to minimize the effects of surface

states on the modulation of the luminescence. GaAs is being grown by means of liquid phase epitaxy from a saturated solution in gallium. Layers in excess of $100\text{ }\mu\text{m}$ thickness have been deposited on $\{100\}$ and $\{111\}$ B faces. Van Der Pauw Measurements at liquid hydrogen temperatures on the best sample to date indicate $\mu = 5,000\text{ cm}^2/\text{v-sec}$ and $n = 10^{17}$. The equipment is being modified to produce better quality GaAs and mixed crystals of $\text{Ga}_x\text{In}_{1-x}\text{As}$.

Since radiative recombination in indirect-gap materials such as silicon is phonon-assisted, it may be possible to enhance the photoluminescence by generating the momentum conserving phonons that are active in radiative transitions. Phonons having the correct crystal momentum can be generated in silicon tunnel diodes at low temperatures. The tunnel diodes are fabricated on a wafer of relatively high resistivity, luminescent silicon by a two-step process in such a way as to minimize the degradation of the photoluminescence. Starting with n-type ($0.1 < \rho < 300\Omega\text{-cm}$), float-zone refined silicon, an n^+ phosphorus layer is diffused at relatively low diffusion temperatures (1050°C) for up to two weeks to achieve the required depth. A thin ($\sim 15\text{ }\mu\text{m}$) aluminum ribbon containing boron is then alloyed into the diffused layer. Tunnel diodes with peak-to-valley ratios of 2.0 and peak tunneling currents of 100 A/cm^2 have been constructed using this technique. Photoluminescence spectra have been measured at 77°K from wafers having tunnel diodes fabricated by the above process. Work is presently underway to measure the proposed photoluminescence enhancement over the temperature range from 2.0 to 40°K .

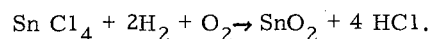
12.0 Study of Stannic Oxide as a High Temperature Semiconductor

Personnel: R. H. Rediker, F. O. Arntz; A. Linz; C. Fonstad

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

At approximately the start of calendar year 1968, a program was initiated to evaluate single-crystal stannic oxide, SnO_2 , as a material for active semiconductor devices that will operate at temperatures in excess of 400°C .

As the first step in this program, single crystals of SnO_2 have been grown. The growing system is based on reacting oxygen, hydrogen, and stannic chloride in a globar furnace at 1250°C at reduced pressure of 10 mm Hg , to produce stannic oxide:



The SnCl_4 which is produced by flowing chlorine through fine mesh tin metal at 100°C is injected into the furnace hot zone as a gas through a zirconium oxide nozzle where it reacts with the other gases. The reaction is controlled by mixing the SnCl_4 before it is injected with excess chlorine and also by adjusting the flow of H_2 which is injected into the furnace as a sheath about the zirconium nozzle. Crystal growth occurs on a quartz linear tube which is slipped inside the mullite furnace tube.

The crystals of SnO_2 which have been grown are clear and transparent. The predominant habit is rods 4-5 mm long with diamond cross-section of 2-3 mm on a side. The rods grow attached at their bases to the liner and grow out into the center of the tube. The crystals are twinned along the long diamond diagonal, a $\{011\}$ face, and the side faces are $\{111\}$. Preliminary electrical measurements indicate that the room temperature resistivity is of the order $10^3 \Omega\text{-cm}$.

13.0 Electrical and Electro-Optical Properties of Heterojunctions

Personnel: R. H. Rediker; J. Womac

Sponsorship: Advanced Research Projects Agency

Heterojunctions between InAs and InSb have been fabricated by an alloy process which involves melting a disc of InSb on top of an InAs wafer and then regrowing the InSb from the InAs. If in this technique the cooling cycle is made abrupt (1 second duration) the heterojunction grows single crystal while if temperature is reduced more slowly the heterojunction becomes polycrystalline. Both photovoltaic measurements as a function of the wavelength of the incident radiation and electrical measurements as a function of temperature have been made on the single-crystal heterojunctions.

Heterojunctions made with n-type InAs have not exhibited significant rectification while those made with p-type InAs with more than 6×10^{17} carriers cm^{-3} exhibited tunnel diode characteristics with a peak to valley ratio of 2.5 and a peak voltage of 0.1v. These results are consistent with an n^+ layer produced in the InAs at the heterojunction interface similar to that produced on an InAs surface by a metallic contact. The InSb used in these heterojunctions has varied from n-type with 10^{14} carriers cm^{-3} to p-type with 3×10^{18} carriers cm^{-3} .

For these same InSb concentrations, junctions made with p-type InAs doped to 1.4×10^{17} cc exhibited a forward I-V relationship of the form $I \propto \exp \frac{qV}{nkT}$ with "n" a function of temperature varying from about 1.3 at 200°K to 2.5 at 77°K. At 4.2°K, "n" is about 70 indicating a field emission through a majority carrier barrier. The reverse I-V characteristics followed a relationship of the form $I \propto V \exp BV$ indicative of reverse band-to-band tunneling.

Photovoltaic measurements at 77°K on these junctions show in addition to the InAs bandgap response, a response below the gap decreasing exponentially with decreasing energy.

Heterojunctions have been annealed for fourteen days at 519°C (6°C below the melting point of InSb) with the goal of producing a more graded single crystal heterojunction. Preliminary photovoltaic measurements at 77°K on these junctions show an additional small response of opposite sign at photon energies near the InSb bandgap. A model has been proposed to explain these results.

14.0 Ion Implantation

Personnel: Dr. F. Rudenauer

Sponsorship: NASA (MIT Center for Space Research), High Voltage Engineering Laboratory Endowment Fund, 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 should make possible important studies in the solid state device field and in the general area of materials science, including surface metallurgy. The unique characteristics of the facility are:

- (1) The capability of implanting atomic particles selected from the entire periodic table in any selected target material.
- (2) Accurate control of the implantation energy over the range of from below 100 KeV to 3 MeV for singly charged ions. Provision will be made for the generation and analysis of multiply charged ions, thus allowing some species to be accelerated up to 6 and 9 MeV (and perhaps higher) at reduced current levels.
- (3) An ion source completely accessible to the operator after a short

(40 minute) procedure. Rapid change will thus be possible of the atomic specie to be implanted. The source will be accessible by degassing and withdrawing the solid dielectric structure which surrounds the electrostatic column, terminal, and acceleration tube assembly.

(4) A target region at ground potential, designed for freedom from contamination, wide range of temperature control, quick access, and accurate geometrical control of the target and the ion beam.

The constructional details of the ion source and mass analyzer section planned for the ion implantation facility have been partially worked out. As mass analyzer a 90° magnetic sector with wedge-shaped pole pieces followed by a 45° spherical electrostatic condenser has been chosen. This arrangement combines high transmission and relatively low weight (ca. 350 pounds) and will allow unit mass resolution at least up to mass number 120. Construction drawings are being made. As ion source, due to the limited amount of power available at the high voltage terminal of the Van de Graaff machine, a source of the Unoplasmatron type has been chosen. It is expected that with a power consumption of about 150 watts, ion currents of the order of a few μ amperes can be produced for most of the elements in the periodic system. A low temperature version of a Unoplasmatron has been built and presently is under test. The first model of this ion source will be delivered to Lincoln Laboratory for use in their 400 KeV Van de Graaff positive ion accelerator.

15.0 Radioactive Tracer Studies of Diffusion in Semiconductors

Personnel: L. L. Chang

Sponsorship: Advanced Research Projects Agency

A program has been initiated to use radio-tracer techniques to study diffusion in semiconductors and a laboratory is being set up for this purpose. The first problem which will be investigated will be the self diffusion of Se and Pb in PbSe. This work on material with controlled deviations from stoichiometry will complement our measurements on the depth of p-n junctions in PbSe and our calculations of the impurity profiles based on the model of Brebrick described in section 10.0. It will also further increase our knowledge of diffusion in the lead salts - a special class of semiconductors that is attracting growing interest.

Theses:

- R. W. Brodersen, "Concentration Dependent Interdiffusion in the Lead Chalocogenides," S.M. and E.E. Thesis, Department of Electrical Engineering, October 1968.
- L. Castro, "Analysis of a Planar Photovoltaic Energy Converter," S.M. Thesis, Department of Electrical Engineering, June 1968.
- R. J. Finke, "Investigation of Anomalous Diffusion of Base Impurities in Three-Layer Silicon Structures," S.M. Thesis, Department of Electrical Engineering, August 1968.
- R. Greischar, "Electrical Properties of GaAs Thin Films," S.M. Thesis, Department of Electrical Engineering, January 1968.
- H. P. Jenssen, "Temperature Dependence of Optically Pumped Semiconductor Lasers," S.M. and E.E. Thesis, Department of Electrical Engineering, January 1968.
- P. C. Lindsey, Jr., "Conductivity Modulation in the Intrinsic Barrier of an Epitaxial Transistor," S.M. and E.E. Thesis, Department of Electrical Engineering, June 1968.
- J. R. Lowney, "Measurement of the Ambipolar Diffusion Coefficient and Incremental Lifetime at High Injection Levels," S.M. and E.E. Thesis, Department of Electrical Engineering, June 1968.
- T. R. Schlax, "A Study of the Potential, Current, and Carrier Distribution within the Transistor Base Region," Ph.D. Thesis, Department of Electrical Engineering, February 1968.
- R. D. Solomon, "A Study of the Limitations on the Packing Density of Integrated Circuits," S.M. Thesis, Department of Electrical Engineering, August 1968.

Publications:

- B. D. Wedlock, R. Siegel, C. R. Hewes, D. L. Smythe, "Investigations of a Pin-Structure Germanium Photovoltaic Cell," Technical Report ECOM 01978-2, June 1967; Semiannual Report 15 July 1966 to 1 February 1967, Contract No. DA-28-043-AMC-01978(E) DA Project No. 1 CO 14501 A 34A, U.S. Army Electronics Command, Fort Monmouth, New Jersey.
- P. E. Gray, J. G. Kassakian, T. Schlax, D. L. Smythe, "Investigation of a Pin-Structure Germanium Photovoltaic Cell," Semiannual Report ECOM 01978-3, November 1967, Contract DA-28-043-AMC-01978(E); Semiannual Report 1 February 1967 to 31 July 1967, DA Project No. 1 TO 14501 A 34A, U.S. Army Electronics Command, Fort Monmouth, New Jersey.

- B. D. Wedlock, "On the Field-Effect Transistor Characteristics, " IEEE Transactions on Electron Devices Volume ED-15, No. 3, March 1968, pp. 181-182.
- R. D. Thornton, "High Frequency Motors for Electric Propulsion," IECEC 1968 Record, pp. 797-803.
- B. D. Wedlock, "Direct Determination of the Pinch-off Voltage of a Depletion-Mode Field-Effect Transistor," to be published in IEEE Proceedings (Letters), December 1968.

IV. MICROWAVE AND QUANTUM MAGNETICS

Faculty:

D. J. Epstein, Professor, Electrical Engineering
F. R. Morgenthaler, Professor, Electrical Engineering
R. Nevald, Assistant Professor, Electrical Engineering (Visiting)

Graduate Students:

D. Bullock, Research Assistant, Electrical Engineering
N. Curland, Research Assistant, Electrical Engineering
H. L. Hu, Research Assistant, Electrical Engineering
Y. S. Lee, Research Assistant, Electrical Engineering
A. Platzker, Research Assistant, Electrical Engineering
L. Tocci, Research Assistant, Electrical Engineering
J. Doane, Graduate Student, Electrical Engineering
W. J. Ince, Graduate Student, Electrical Engineering,
Lincoln Laboratory Staff Associate
D. Pearson, Graduate Student, Electrical Engineering
E. Venturini, Graduate Student, Electrical Engineering
K. B. Kanarek, Undergraduate Student, Electrical Engineering

Support Staff:

Barbara Baldassarre, Secretary, Electrical Engineering (to March 1968)
Elaine Imbornone, Secretary, Electrical Engineering (from March 1968)

Personnel who have left:

W. E. Courtney, DSR Staff, Electrical Engineering (Now with Lincoln Laboratory)
S. Rezende, Research Assistant, Electrical Engineering (Now Assistant Professor of Physics, Catholic University, Rio de Janeiro, Brazil)

Degrees Granted:

S. Rezende, Ph.D., Electrical Engineering, February 1968
E. Venturini, S.M., Electrical Engineering, August 1968
M. Zahn, S.M., Electrical Engineering, June 1968
D. Fye, S.B., Electrical Engineering, June 1968
M. Thomas, S.B., Electrical Engineering, June 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75113, 75116
 Air Force Cambridge Research Laboratories, AF 19(628)-5876,
 DSR 76282

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

Research Report

The work of the Microwave and Quantum Magnetics Group is directed toward elucidating and exploiting those features of magnetic insulators which may lead to novel applications in the field of microwave and quantum electronics. Specific studies include the investigation of microwave loss mechanisms, photomagnetic effects, coupled nuclear and electron resonances, quasiparticle interactions among magnons, phonons, and photons. Areas of application include microwave absorbers, micro-miniature microwave devices, tuneable delay lines, magnetoelastic parametric amplifiers, pulse compression filters and magneto-optical devices.

1.0 Resonance Losses in Garnets

Personnel: D. J. Epstein; L. Tocci

We have proposed that resonance losses observed in Si-YIG above room temperature can be attributed to a 4-level valence-exchange mechanism. We have previously shown that this model correctly describes the functional form of the anisotropic loss we have observed in the (110)-plane. To check the internal consistency of our model we have recently examined the anisotropy in the (112)-plane. The observed angular dependence is in excellent agreement with our theoretical calculations. We have also begun to examine the effect of changes in saturation magnetization on the linewidth. The valence-exchange model predicts that the linewidth should increase as M^{-1} . To vary M we plan to substitute Ga for Fe in YIG. Some initial measurements have been made on a sample in which about 12% of the iron atoms have been replaced by gallium. In order to be able to follow the M dependence of the linewidth it will be necessary to have accurate knowledge of the silicon impurity concentration and to know M as a function of T for a controlled series of doped samples.

2.0 Photomagnetic Effects in Silicon Doped YIG

Personnel: D. J. Epstein; D. Bullock

We have begun to investigate the effect of infrared radiation on the low temperature resonance behavior of Si-YIG single crystals. The nature of our basic experiment is as follows. A spherical sample of Si-YIG is mounted on a post in a 12.9 GHz rectangular wave-guide cavity, oriented so that it can be rotated in the (110)-plane relative to an external d.c. magnetic field. The d.c. field is initially applied along the [111] direction at room temperature, the sample is cooled in this field to 77°K and the field for resonance is measured. The sample is then rotated to $[1\bar{1}\bar{1}]$ which normally would be an entirely equivalent direction. However, the equivalence is destroyed by magnetic anneal effects and, consequently, there is a shift in field for resonance followed by a relaxation toward equilibrium as the sample reanneals in the new direction. Preliminary measurements show that illumination of the sample by infrared radiation near the absorption edge accelerates the approach to equilibrium.

Application of the illumination technique will enable us to study the intrinsic linewidth at low temperature, something which we have been unable to do previously because of the metastabilities resulting from magnetic anneal.

3.0 Conductivity in Garnets

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

An a.c. Hall apparatus has been constructed for the measurement of the ordinary and extra-ordinary Hall coefficients of samples of silicon doped YIG.

As a check on the performance of the equipment we have measured the Hall effect in nickel-ferrous-ferrite, a material which has previously been examined by a number of workers. Our data is in excellent agreement with the published results.

Measurements on Si-YIG have been started. Both the ordinary and extra-ordinary Hall coefficients are negative, indicating n-type behavior as anticipated.

4.0 Thin Film Magnetic Oxides

Personnel: R. Nevald

Thin magnetic-oxide films have considerable potential for miniaturized microwave and magnetoelastic devices. In order to pursue possibilities in this direction we have undertaken to develop a facility for the fabrication of crystalline thin films by the method of chemical vapor deposition. Design of the furnace and gas flow apparatus is under way.

5.0 Magnetic and Elastic Studies of the Antiferromagnet RbMnF_3

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

5.1 Coupled Electronic and Nuclear Modes

W. J. Ince has for his doctoral dissertation carried out a theoretical and experimental investigation of dynamically coupled nuclear electronic spin resonance of Mn^{2+} in RbMnF_3 . The theory differs from that of previous investigations, which assumed that the nuclear spins are unable to follow the precessional motion of the electrons. In general, the complexity of the dynamically coupled resonance analysis is only warranted if the electronic and nuclear normal mode frequencies are close. However, in RbMnF_3 it is shown that there is significant deviation in the frequencies calculated by the two approaches for certain crystal orientations and field strengths. Greatest deviation occurs when the magnetizing field is parallel to a $[110]$ direction and when the spins are almost flopped.

Electron-nuclear double resonance has been observed in RbMnF_3 at liquid helium temperatures. Nuclear saturation, which was induced by applying a large amplitude UHF signal to the sample, was detected as a shift in the field required for AFMR at x-band frequencies. With the field applied in the $[100]$ direction, saturation could be induced by pumping either the low field or spin flop modes. For a given x-band frequency, the effective nuclear temperatures for the low field and spin flop modes were in substantial agreement. The range of pumping frequency over which saturation could be induced was roughly 100 MHz, (≤ 686 MHz), and was a function of the Mn^{55} resonant frequency. Extrapolation of the experimental data to infinite nuclear temperature yields a value of 686.5 MHz for the unpulled nuclear hyperfine frequency, which agrees well with the value

obtained from direct NMR experiments. Measurements of the saturation decay yielded a value of 55.5 msec for T_1 at 4.2°K.

5.2 Antiferromagnetic Domains

W. J. Ince and A. Platzker have reported on the indirect observation of domains in RbMnF_3 through antiferromagnetic resonance. The probable orientations of domains have been calculated for the case of a magnetic field applied along the $[11\bar{2}]$ direction. There is good agreement between calculated resonant frequencies for the domains as a function of applied field and the experimentally observed values.

5.3 Phonon-Pumped Magnons in an Antiferromagnet

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

6.0 Frequency and Mode Conversion of Velocity Modulated Magneto-elastic Waves

Personnel: F. R. Morgenthaler; B. Hu; E. Venturini

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 converted from magnon-like to phonon-like (or vice versa) by suitable time and/or space variation of the bias field; such frequency and/or mode conversion can be utilized in fundamental spectroscopy as well as in the field of microwave ultrasonic devices.

Mr. B. Hu is presently setting up an optical bench so that he can use 1.14 micron radiation from a He-Ne laser as a probe to study the dynamics of the conversion process.

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 considered. The simultaneous presence of evanescent and propagating waves can, under suitable circumstances, lead to direct transfer of power between the electromagnetic, exchange, and elastic channels.

J. Doane has undertaken 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 that better excitation schemes could be developed as a result. The effect of magnetic loss on the excitation process is perhaps the least-well understood aspect of the problem, and will be treated first. This treatment will involve the study of dispersion relations with loss, and the study of how loss affects the WKB solutions for waves in a nonuniform magnetic field. The properties of magnetostatic waves and spin waves in nonuniform fields will also be studied, with the objective of calculating their excitation by a fine wire antenna. Finally, the study will investigate the possibility that conversion from electromagnetic energy to magnetoelastic energy occurs through the electromagnetic power rather than the exchange power of spin waves.

8.0 Nonlinear Saturation of Magnetoelastic Waves

Personnel: F. R. Morgenthaler; N. Curland

Nonlinear saturation of magnetoelastic waves due to parametrically induced instabilities has been studied experimentally in YIG. A movable fine wire probe was used to excite and detect quasi-static wave packets. Saturation effects were studied as a function of bias field, pulse duration and crystal orientation. The results are summarized in the soon to be completed S.M. thesis of N. Curland.

Theses:

- S. M. Rezende, "Magnetoelastic and Magnetostatic Waves in Time-Varying Magnetic Fields", Ph.D. Thesis, Department of Electrical Engineering, February 1968.
- M. Zahn, "Pulse Compression Using Bragg Scattering of Light by Ultrasonic Waves", S.M. Thesis, Department of Electrical Engineering, June 1968.
- E. Venturini, "Optical Beam Diffraction from Acoustic Waves: Elasto-Optic Constants of Four New Single Crystals", S.M. Thesis, Department of Electrical Engineering, August 1968.
- D. Fye, "Construction of a YIG Delay Line with Adjustable Time Delay", S.B. Thesis, Department of Electrical Engineering, June 1968.
- M. Thomas, "Microwave Electromagnetic Propagation in Ferrites", S.B. Thesis, Department of Electrical Engineering, June 1968.

Publications:

- D. J. Epstein, "Comment on a Theorem in the Field of Steady Current Flow", Proc. IEEE 56, 198 (1968).
- P. H. Cole, "Interpretation of Parallel Pumping Experiments Near the Magnetoelastic Interaction Region", IEEE Transactions on Magnetism, 4, 2, June 1968.
- W. J. Ince, "Electron-Nuclear Double Resonance in RbMnF_3 ", to be published in Physical Review.
- W. J. Ince and J. S. Friebely, "Properties of the Compounds RbMnF_3 , KMnF_3 and CsMnF_3 ", Lincoln Laboratory Report ESD-TR-68-240, August 8, 1968.
- W. J. Ince and A. Platzker, "Antiferromagnetic Domains in RbMnF_3 ", to be published in Physical Review.
- S. M. Rezende and F. R. Morgenthaler, "Magnetoelastic Waves in Time Varying Magnetic Fields I. Theory; II. Experiments, to be published in the Journal of Applied Physics, February 1969.

V. CRYSTAL PHYSICS AND OPTICAL ELECTRONICS LABORATORY

Faculty:

A. Smakula, Professor, Electrical Engineering

Research Staff:

A. Linz, Research Associate, Electrical Engineering

J. Kalnajs, Research Physical Chemist, DSR Staff

D. Gabbe, DSR Staff (part-time)

R. Mykolajewycz, DSR Staff (on leave of absence since January 1968)

E. F. Farrell, DSR Staff

V. Belruss, DSR Staff

Graduate Students:

T. G. Davis, Research Assistant, Electrical Engineering

T. M. Grove, Graduate Student, Electrical Engineering

S. L. Markowitz, Graduate Student, Electrical Engineering

P. C. M. Munasinghe, Research Assistant, Electrical Engineering

R. A. Schaffzin, Teaching Assistant, Electrical Engineering

N. Skribanowitz, Graduate Student, Physics Department

A. Houshmand, Senior Thesis Student, Electrical Engineering

Support Staff:

R. Mills, Project Technician

A. Vetrovs, Technical Assistant

Delphine Radcliffe, Secretary

Personnel who have left:

A. Houshmand, Senior Thesis Student, E. E. (Now at Carnegie Institute of Technology)

S. L. Markowitz, Graduate Student, E. E.

Degrees Granted:

T. G. Davis, Ph. D., Electrical Engineering, September 1968. (Now Assistant Professor, Electrical Engineering, MIT)

A. Houshmand, S. B., Electrical Engineering, June 1968.

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75111, 78894

Office of Naval Research, Nonr-3963(20), DSR 74638

Office of Naval Research, N00014-67-A-0204-0025, DSR 71101

U. S. Air Force, Wright-Patterson AFB, Avionics Laboratory,
F33615-68-C-1490, DSR 70963

U. S. Army Engineers, RDL, DA-44-009-AMC-1117(T), DSR 74950 (term.)

MITHRAS, Div. of Sanders Associates, DSR 70757 (term.)

Research Report**1.0 Crystal Growth**

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

1.1 Ferroelectric Crystals

Crystals of oxide perovskite ferroelectrics such as BaTiO_3 , $(\text{K}, \text{Na})\text{TaO}_3$, were grown by the top-seeded solution growth technique using an excess of one constituent as a solvent. A program has been initiated to adapt the technique to the growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, an oxygen octahedra type ferroelectric with a complex layer structure. This structure makes growth difficult by introducing a "platey" habit. We are also studying the growth of $\text{Gd}_2(\text{MoO}_3)_4$, a low dielectric constant ferroelectric which appears to have soft acoustical shear mode.

1.2 Germanates

A number of rare earth doped crystals of $\text{Ba}_2\text{MgGe}_2\text{O}_7$ have been grown by the top-seeded solution technique for laser host studies. Other complex germanate and silicate systems are being investigated as possible host materials for optically pumped rare earth lasers.

1.3 Magnetic Oxides

Application of the top-seeded solution technique to the growth of yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) from an excess of Fe_2O_3 was attempted. Preliminary results were encouraging, indicating that the technique is feasible if high-purity feed materials can be obtained.

1.4 High Temperature Oxides

A high temperature RF induction heated Czochralski furnace has been set up and used initially for the growth of CaWO_4 and other scheelite structure crystals. Modifications are still being made to the apparatus, and eventually it is expected that crystals with melting points between 1400°C and 2100°C can be grown under various atmospheres. These modifications include decreasing the temperature gradients sufficiently to permit high temperature growth by the top-seeded solution technique at temperatures in excess of 1500°C , the current limit for our glow-bar heated TSSG furnaces. In the meantime, the furnace has been used to grow a number of CaWO_4 crystals, both high purity and containing deliberate doping agents such as Ti, Pb, Nb, and Ta. These crystals were needed for spectroscopic investigations. Work has been initiated on the growth of olivine, Mg_2SiO_4 , as a prototype for the growth of complex silicates.

A number of crystals of CoO and NiO, specially oriented, were grown upon request. Use has also been made of the furnace by students for the growth of Al_2O_3 crystals with various impurities for diffusion studies.

1.5 Fluorides

1.5.1 Zone Refining

Purity of feed material is the most important problem in the fluoride growth area. A simple high-temperature zone refiner has been operated for some time in order to develop design criteria for construction of a unit which will make possible routine purification of fluoride feeds without recontamination from materials used in the refiner. These experiments have been concluded and work is beginning on the design of the equipment

1.5.2 Manganous Fluorides

A number of crystals of RbMnF_3 doped with from 500 to 2000 ppm

Co were grown for magnetic resonance and anisotropy measurements. Pure crystals of extremely high optical clarity were also grown for Brillouin scattering experiments. Several crystals of MnF_2 were grown for neutron diffraction studies. These crystals are required to be relatively strain-free and to exhibit a minimum of mosaic spread.

1.5.3 Rare Earth Fluorides

A number of crystals of LiYF_4 with one or more rare earth dopants were grown for laser host studies. Work is continuing on other isomorphous materials, including LiGdF_4 and LiErF_4 .

1.6 Growth of Thiospinels

Ternary sulfide, selenide and telluride crystals have been gaining interest in recent years for fundamental research and possible application as window materials for infrared, photodetectors, direct gap emitters, ferromagnetic semiconductors, etc. The crystals presently available are too small for general characterization and not pure enough for practical application.

The principal aim of this investigation is to grow ternary crystals such as CdY_2S_4 , CdIn_2S_4 and related materials. The only known method for growing crystals of these materials is by chemical transport reaction. (R. Nitsche, H. U. Bölscherli and M. Lichtensteiger, J. Phys. Chem. Solids 21, 199 (1961).) The method utilizes formation of an intermediate gaseous compound from solid and gas. This gaseous compound either decomposes at lower temperatures at the opposite end of the reaction vessel, or reacts with other material to form binary or ternary systems.

This method has been used to grow CdIn_2S_4 from $\text{CdS} + \text{In}_2\text{S}_3 + \text{I}_2$. Electronic grade CdS was used without further purification. The purchased In_2S_3 was recalcined in dry H_2S at 400°C . Well developed deep red octahedral crystals up to 6 mm in size were obtained. Our preliminary attempts to obtain larger crystals were not successful.

There are too many parameters involved in the growth process which are not established, such as starting material (amount and purity), composition, dimensions of the reaction vessel, temperature and its gradient.

A more versatile furnace has been ordered which should speed up the research and aid in determining optimal conditions for growing larger and more perfect crystals of CdIn_2S_4 . When this is achieved we will expand our endeavours to other materials.

2.0 Crystal Research

Personnel

A. Smakula, D. J. Epstein, A. Linz, J. Kalnajs, E. Farrell
T. G. Davis, T. M. Grove, P. C. M. Munasinghe, R. A. Schaffzin,
N. Skribanowitz, A. Houshmand, A. Vetrovs

2.1 Crystal Structure Models (E. Farrell and A. Vetrovs)

During the year we designed and constructed six crystal-structure models of the various high-pressure phases of ice. These included Ice I hexagonal, Ice I cubic, Ice II, Ice III, Ice VI and Ice VII. The oxygen structure of Ice I hexagonal was first determined by Barnes. Pauling determined the H positions by utilizing data of residual entropy. Neutron diffraction studies by Wallon et al. on powdered ice and by Peterson and Levy on single crystals of D_2O confirmed Pauling's model.

Cubic Ice I was discovered by König with electron diffraction, while Whalleyvass and Carpenter produced Ice I cubic by low temperature condensation. Ice I cubic was found to have the diamond structure.

Tammann discovered Ice II and III, while Bridgman found Ice IV, V, VI and VII. Little is known concerning the proton distribution in any of these phases, except for Ice II (Kamb), which is fully ordered. Ice II has a rhombohedral unit cell whose structure consists of Ice I like

units built out of puckered six-rings of water molecules. Each neighbor has four nearest neighbors at 2.80 Å with a next nearest neighbor at 3.24 Å. Ice III (Kamb and Datta) is dimensionally cubic but structurally tetragonal, $a = c = 6.80$ Å. The structure is similar to the positions for Si in Keatite, a high-pressure polymorph of SiO_2 .

Ice IV is a glass which represents an unstable transition to Ice V, whose structural details are not fully known. Ice VI tetragonal consists of hydrogen bonded chains of water molecules analogous to the tectosilicate chains which constitute the fibrous zeolites. These chains interpenetrate but do not interconnect and in that sense are self clathrates which achieve high density.

Ice VII is cubic and represents the ultimate close packing and thus the densest structure in the ice series. The Ice VII structure consists of interpenetrating but not interconnecting frameworks of Ice I. The density should be twice that of Ice I, but the O - O lengths are stretched out to 2.86 Å in Ice VII (at 25 K bars) compared with 2.76 Å in Ice I.

2.2 Crystal Field Spectra and Dichroism of Tourmaline (E. Farrell)

Tourmaline is a silicate mineral whose physical and optical properties have made it a useful device. Its absorption properties make it an absorption polarizer, while its piezoelectric properties have been utilized as pressure gauges for the measurement of sudden, large hydrostatic pressures.

The optical absorption spectra of colorless, pink, green, brown and black tourmaline have been taken to determine the origin of the colors and to explain the color changes which occur on heating. Absorption data were taken with polarized radiation parallel and perpendicular to the c axis at 77°K and 300°K. Cell dimensions supported by partial chemical analyses were used to characterize the specimens.

The data combined to show that generally speaking the color is due to electronic transitions in, and the amount of, Fe^{2+} , Fe^{3+} and Mn^{2+} in the crystal. Specimens on the dravite-schorl join are characteristically colored shades of brown. With small to moderate concentrations of transition metal ions, colors on the elbaite-schorl join are clear pinks, greens and blues according to the $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+})$ ratio in the tourmaline.

Intensity changes of absorption peaks and shifts in the absorption edges, correlated with removal of hydrogen and consequent oxidation of Fe^{2+} to Fe^{3+} in the structure, account for color changes observed when tourmaline is heated in air. Blue tourmaline becomes green on short-term heating and reddish-brown on further heating. Assignments of absorption peaks from 0.3 to 2.0 microns to specific transitions in the appropriate cations have been made and an explanation of the origin of the characteristic dichroism has been given.

2.3 Ferroelectric Studies

2.3.1 Ferroelectric Phonon Modes in Sodium Tantalate-Potassium Tantalate Mixed Crystals (T. G. Davis)

Mixed crystals in the $(\text{K}, \text{Na})\text{TaO}_3$ system have been grown with compositions ranging from KTaO_3 to $(0.10 \text{ K}, 0.90 \text{ Na})\text{TaO}_3$. The dielectric phase diagram has been determined for the composition range KTaO_3 to $(0.30 \text{ K}, 0.70 \text{ Na})\text{TaO}_3$. For compositions containing less than 50% NaTaO_3 , the Curie temperature increases monotonically with sodium concentration to a maximum value of 65°K . Samples containing between 30% and 50% NaTaO_3 undergo two transitions, the lower temperature one being a transition to another ferroelectric phase of different symmetry. Samples containing more than 50% NaTaO_3 appear to undergo transitions from the paraelectric phase directly into the second ferroelectric phase of lower symmetry, and the Curie temperature decreases with further increase in sodium concentration.

The Curie temperature is below liquid helium for the composition (0.28 K, 0.72 Na)TaO₃. Compositions containing more than 84% NaTaO₃ show optical domain structure, but no dielectric hysteresis; they do not undergo ferroelectric transitions, but do have weak Curie-Weiss behavior of the dielectric constant.

In the paraelectric phases of all the samples undergoing ferroelectric transitions, "soft" transverse optical modes have been observed by means of electric-field induced Raman scattering. The mode line shapes could not be accurately described by the usual damped harmonic oscillator response function. An empirical form containing only one parameter was found to describe accurately the mode profiles for all compositions. The Cochran relation, $\omega = c/\sqrt{\kappa}$, was found to be obeyed closely in all cases. The constant c decreased monotonically from 1.30×10^3 mks for KTaO₃ to 1.10×10^3 for the composition (0.40 K, 0.60 Na)TaO₃. The damping became increasingly larger, and the scattering efficiency smaller, with increasing sodium concentration.

Electric-field dependence of the small-signal dielectric constant and mode frequencies were not well correlated. In all cases the field dependence of the mode frequency was higher than expected on the basis of dielectric constant measurements; and higher order terms in the Devonshire expansion were required to describe the optical mode behavior. The damping constant was found to be independent of field for all compositions.

Observations of the soft modes in the polar phase gave estimates of spontaneous polarization in fair agreement with values measured from hysteresis loops. Soft modes were also observed in field-induced scattering from the non-cubic samples of high sodium concentration which do not undergo ferroelectric transitions.

2.3.2 Conduction in Barium Titanate (D. J. Epstein, T. Grove)

Doped barium titanate ceramics are known to exhibit an anomalous resistance variation with temperature in the vicinity of the Curie point (PTC effect) as well as unusual volt-ampere characteristics. It has been suggested that these effects are a result of depletion layer barriers at grain boundaries. In order to explore the essential features of this model in a controlled way, we plan to investigate surface barriers on semiconducting samples of barium titanate. Present studies are concerned with metal-semiconductor contacts on hydrogen reduced barium titanate. This work will eventually be extended to doped crystals.

2.3.3 Electro-Optical Deflectors (A. Linz, R. Schaffzin)

Use of BaTiO_3 above its Curie temperature as a quadratic electro-optical deflector appears possible. Advantages and limitations of a practical system are being studied and a prototype scanner has been designed and is under construction.

2.4 Influence of Temperature on Luminescence in Ferroelectric and Antiferromagnetic Crystals (A. Smakula, A. Linz, J. Kalnajs)

Luminescence in crystals with perovskite structure was investigated as a function of temperature and dielectric constant. Crystals of KTaO_3 , KTN, BaTiO_3 , SrTiO_3 , RbMnF_3 , CsMnF_3 and MnF_2 were studied, and activators of Mn, Eu, Sm and Cr were used. The crystals were grown and their optical absorption and dielectric constant were measured.

KTaO_3 crystals doped with MnCO_3 did not show any luminescence at 77°K and 300°K , although a broad absorption band at 4150 Å indicates that some Mn is incorporated in the crystal. Crystals doped with Eu_2O_3 showed a strong luminescence between 5400 Å and 6600 Å, consisting of four groups of emission bands. The luminescence intensity increased strongly with decreasing temperature, reaching a plateau below 150°K . Simultaneous doping with Eu_2O_3 and MnCO_3 gives, at 300°K , only Mn luminescence with a peak at 7,000 Å. At 77°K emission of Mn increases

and in addition the emission of Eu appears superimposed on the Mn emission band.

KTaO_3 crystals doped with Cr did not show any emission. Simultaneous doping with Eu and Cr showed a strong increase of Eu emission but no Cr emission could be detected.

In mixed crystals of $\text{KTaO}_3\text{-KNbO}_3$ (= KTN) doped with Eu, the same emission as in KTaO_3 was observed. Crystals containing Eu and Mn showed only Eu emission. Luminescence spectrum of Sm in KTN is similar to that in KTaO_3 , except that a few additional lines appear. No anomaly of luminescence has been detected at temperatures where ferroelectric transitions take place.

Polycrystalline BaTiO_3 doped with Sm shows a strong luminescence below 220°K . No emission has been observed in single crystals doped with MnCO_3 either below or above the Curie temperature at 130°C where the variation of dielectric constant is very high. Strong emission has been observed in undoped SrTiO_3 below 200°K . The intensity of emission increases strongly with decreasing temperature down to 100°K . An extremely sharp decrease of intensity below 100°K has been reported by Sihvonen. No dielectric anomaly could be detected in this temperature region.

A sharp spectral shift of the 6250 Å emission band in RbMnF_3 at 35°K observed by Holloway et al. could not be verified. Instead, the development of a new band at 5900 Å was detected, which probably simulated a shift of the 6250 Å band.

In CsMnF_3 also two emission bands were observed, but much weaker than in RbMnF_3 .

In MnF_2 only one broad emission band was observed below 200°K . The emission peak shifted from 6830 Å at 200°K to 6420 Å at 30°K . The halfwidth increases with decreasing temperature by about 50% between 200 and 100°K . It is possible that there are two strongly overlapping

bands as in RbMnF_3 .

2.5 Dielectric Spectroscopy of Silicon (A. Smakula, N. Skribanowitz)

In our previous investigation (K. V. Rao and A. Smakula, J. Appl. Phys. 37, 2840 (1966)) of dielectric properties of single crystals at frequencies $10^2 - 10^{10}$ cps in the temperature range between liquid He and several hundred $^\circ\text{K}$ we found anomalous dielectric behavior of silicon at low temperatures around 30°K . Below 30°K the dielectric constant κ' is equal to the square of the refractive index n . Around 30°K the dielectric constant jumps to a higher value. The jump occurs always at the same temperature, but the height of the plateau varies linearly with the square root of the sample conductivity.

Although the dielectric anomaly of Si can be explained by the presence of impurities or other defects, additional experimental data are required for a full understanding. Therefore we continued our study in more detail under improved experimental conditions. A new sample holder was built with which the sample can be kept under vacuum or in a protective atmosphere (N_2 , He). A heating device with a very sensitive thermosensor was installed for more accurate temperature control of the sample. The temperature can be measured now with an accuracy of $\pm 0.1^\circ\text{K}$.

For the new study an n-type Si sample with a resistivity of 14,000 ohm cm at room temperature was used. Al or Ni + Au electrodes gave reproducible results. The dielectric constant and loss were measured at frequencies from 40 to 10^5 cps. The dielectric constant had a value of 12 at all frequencies below 19°K . The start of the sharp dielectric constant increase showed a shift from 18°K for 40 cps to 26°K for 10^5 cps. The saturation value of κ' (≈ 36) was the same for all frequencies, but the rate of rise decreased with frequency. The dielectric loss maxima shifted parallel with the change of κ' with

temperature and frequency. The height of the κ' jump depended also on the sample thickness, and was directly proportional to the thickness.

The anomalous dielectric behavior of Si can be explained by the presence of impurities. At temperatures below 19°K the impurities are neutral and their contribution to the dielectric constant is negligible. In this temperature region Si behaves as an ideal monoatomic covalent crystal which has electronic polarization only. Indeed, the dielectric constant, $\kappa' = n^2 = 12$, is as it should be. Above 19°K the neutral impurities become ionized and the charge carriers contribute to the dielectric constant according to their concentration. The concentration of the carriers will depend on the rate of their formation and recombination. According to Macdonald (J. R. Macdonald, Phys. Rev. 92, 4 (1953)) the low frequency dielectric constant will increase linearly with the thickness of the crystal and with the square root of the charge carriers. Both effects have been observed experimentally. The saturation value of the dielectric constant between 25 and 35°K is reached when all impurities are ionized. The increase of κ' at still higher temperature is connected with the ionization of silicon atoms.

Similar anomalies have been obtained in Ge, III - V semiconductors (e.g. GaAs) and II - VI semiconductors (e.g. CdS).

2.6 Optically Pumped Laser Research (A. Linz, J. Kalnajs, M. Munasinghe)

Two new host crystals have been developed for rare earth doped optically pumped lasers and energy transfer studies are in progress. Broad band sensitizers such as transition metal ions and lattice defects are being investigated. Laser test equipment has been added to the facilities of the laboratory.

2.6.1 Lithium Yttrium Fluoride (LiYF₄)

LiYF₄, a scheelite structure crystal, has the advantage of a

large pumping window in the near ultraviolet for excitation of rare earth lines in the visible from dopants such as Tb^{3+} and Eu^{3+} . Since no charge compensation is required for rare earth substitution, the lines remain narrow and large amounts of rare earth sensitizers such as Gd^{3+} can be incorporated. LiYF_4 has proven to be a high gain laser material at $1.06\ \mu$ when doped with Nd^{3+} (Harmer et al., Bull. Am. Phys. Soc. 12, 1068 (1967).) and has also been shown to be a very efficient host for Ho^{3+} at $2.07\ \mu$, particularly when sensitized with Er^{3+} and Tm^{3+} , i. e. $\text{Li}(\text{Y}_{1-x-y}\text{Er}_x\text{Tm}_y)\text{F}_4\text{-Ho}^{3+}$. Large crystals of this material have been grown and the long lifetime of the excited Ho^{3+} level at room temperature suggests higher efficiencies at higher operating temperatures than is currently possible with Er^{3+} sensitized yttrium aluminum garnet, $((\text{Y}, \text{Er}, \text{Tm})_3\text{Al}_5\text{O}_{12}\cdot\text{Ho}^{3+})$. Er^{3+} activated laser action at $1.54\ \mu$ appears hopeful for similar reasons. Detailed lifetime and excitation studies on these various systems are in progress.

2.6.2 Complex Oxides

$\text{Ba}_2\text{MgGe}_2\text{O}_7\cdot\text{Nd}^{3+}$ is an akermanite structure oxide host which has lased with relatively high efficiency and a relatively long lifetime (ca. $450\ \mu\text{s}$). The pseudo-layer structure of this material results in very high dichroism, so that with an 'a' axis rod, completely linearly polarized laser radiation is obtained. This characteristic is very useful in enhancing contrast in night vision applications. Studies of this material with other dopants is in progress. Related materials such as $\text{Ba}_2\text{ZnGe}_2\text{O}_7$ and chemically similar glasses are also under study.

2.6.3 Broad Band Sensitizers

Broad band blue fluorescence has been observed in CaWO_4 , both in "pure" samples and when doped with Pb, Ta, Nb or Mo. This fluorescence has a short lifetime ($< 50\ \mu\text{sec}$) and is being studied as a sensitizer for rare earth ions such as Tb^{3+} and Eu^{3+} .

2.6.4 Instrumentation

Some of our new laser materials can now be grown with sufficiently good optical quality and large enough size for meaningful laser measurements. A test set-up was designed and built for this purpose.

The basic design permits the testing of laser rods of up to 1 cm diameter and 7.5 cm long in a diffuse cavity. The close coupled pump source is an E. G. and G. xenon flashlamp which has a maximum energy output of 400 joules, and a pulse width varying from 150 to 1000 microseconds. The laser can be manually flashed at up to 2 pulses per minute with forced air cooling. Facilities for automatic triggering are available. An interchangeable set of end mirrors permits the investigation of all wavelengths from the visible to the near infrared. Alignment of the optical system is facilitated by an auto-collimator. The design lends itself to easy modification both for increasing the capacity of system (viz. power, rod size, etc.), and for testing a number of solid state materials under varying ambient conditions. By substituting a quartz iodine lamp, the unit may be used for continuous or quasi-continuous operation.

The testing rig has three main component sections:

1. Power supply, including triggering and pulse shaping circuits.
2. Laser cavity and associated optics.
3. Pulse detection and measuring system.

The chief design limitation is set by excessive heating of the laser cavity and rod, even with forced air cooling. Hence the power circuit time constants were chosen to ensure that the upper limit for the pumping rate would be 2 pulses per minute at 400 joules per pulse.

2.7 Density Defects in Single Crystals of Barium Titanate (Smakula, Houshmand)

Differences in density, dielectric constant, and absorption coefficients have been observed between BaTiO_3 grown from a non-

stoichiometric melt of 70% TiO_2 and 30% BaO , and BaTiO_3 grown by the butterfly-wing method. An attempt was made to determine whether these differences are due to an excess of TiO_2 in the crystalline form. The density of BaTiO_3 grown from a nonstoichiometric melt was measured by hydrostatic weighing. The x-ray density was also determined. It was found that the weighing density is lower than the x-ray density. From this it was concluded that either there are lattice vacancies in the crystal, or that the lower density is due to imperfections coming from the 130°C phase transition to the polydomain ferroelectric state.

Theses

- T. G. Davis, "Ferroelectric Phonon Modes in Sodium Tantalate-Potassium Tantalate Mixed Crystals", Ph. D. Thesis, Department of Electrical Engineering, August 1968.
- A. Houshmand, "Density Defects in Single Crystals of Barium Titanate", S. B. Thesis, Department of Electrical Engineering, June 1968.

Publications

- F. Martino, "Localized Impurity States in the Hartree-Fock, LCAO Approximation. I.", Internat. Journ. Quantum Chem., Vol. II, 217-232 (1968).
- F. Martino, "Localized Impurity States in the Hartree-Fock, LCAO Approximation. II. The F Center in KCl ", Internat. Journ. Quantum Chem., Vol. II, 233-263 (1968).
- A. Smakula, "Defects in Crystal Growth of Transition Metal Oxides" in Anisotropy in Single Crystal Refractory Compounds, Vol. 2, p. 27, edited by F. W. Vahldiek and S. A. Merson, Plenum Press, New York, 1968.

Accepted for Publication

- R. W. T. Wilkins, E. F. Farrell and C. S. Naiman, "The Crystal

Field Spectra and Dichroism of Tourmaline". Submitted July 1968 to J. Phys. Chem. Solids.

F. M. Lay, "Fluorescence of Europium and Samarium Ions in Potassium Tantalate and Mixed Crystals of Potassium Tantalate-Potassium Niobate". Submitted July 1968 to J. Phys. Chem. Solids.

D. Gabbe and A. L. Harmer, "Scheelite Structure Fluorides: The Growth of Pure and Rare Earth Doped LiYF_4 ". Submitted October 1968 to Journ. Cryst. Growth.

Papers Presented at Meetings

C. S. Naiman, E. Farrell, A. Linz and J. Kawamura, "The Optical and Fluorescent Properties of Cr-Doped Flame Fusion Spinel", American Physical Society Meeting, Berkeley, March 1968.

Y. Yamada, G. Shirane, and A. Linz, "Critical Fluctuations in BaTiO_3 ", American Physical Society Meeting, Washington D. C., April 1968.

C. S. Naiman, R. W. T. Wilkins and E. F. Farrell, "Interpretation of the Dichroism of Tourmaline", American Physical Society Meeting, Washington D. C., April 1968.

A. S. M. Alam, K. H. Goen, B. Di Bartolo, A. Linz and E. Sharp, "Fluorescence Characteristics of a Crystal $\text{Ba}_2\text{MgGe}_2\text{O}_7$ Doped with Nd", American Physical Society Meeting, Washington D. C. April 1968.

K. Goen, B. Di Bartolo, M. Alam, R. C. Powell, and A. Linz, "Temperature Effects on the Fluorescence Characteristics of $\text{RbMnF}_3:\text{Nd}^{3+}$ ", International Quantum Electronics Conference, Miami, May 1968.

C. S. Naiman, E. Farrell, A. Linz and J. Kawamura, "The Optical and Fluorescent Properties of Cr-Doped Flame Fusion Spinel", International Quantum Electronics Conference, Miami, May 1968.

A. Smakula, "Dielectric Properties of Single Crystals", Electrochemical Society Meeting, Boston, May 1968.

Reports

Final Report on Contract No. AF.19(628)-395: "A Study of the Physical Properties of High-Temperature Single Crystals", September 30, 1967.

Quarterly Technical Reports Nos. 9 and 10 on Contract DA-44-009-AMC-1117(T): "Research on Methods of Obtaining Luminescence in Ferroelectric Materials and Study of the Temperature Dependence of their Luminous Efficiencies close to the Curie Point" for inclusive period July 1, 1967 - December 31, 1967.

Final Technical Report on Contract DA-44-009-AMC-1117(T):
"Research on Methods of Obtaining Luminescence in Ferroelectric Materials and Study of the Temperature Dependence of their Luminous Efficiencies close to the Curie Point", September 23, 1968.

Semi-Annual Status Reports on Contract Nonr-3963(20): "Growth and Study of Certain Perovskite-Structure and Related Laser Host Crystals" for periods April - September, 1967, and October 1967 - May 1968.

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, Graduate Student, Electrical Engineering

M. D. Brody, Graduate Student, Electrical Engineering

Support Staff:

D. K. Owens, Undergraduate Student Technician, Physics

Deborah E. Card, Secretary, Electrical Engineering

Personnel who have left:

H. Wilhelmsen (Now at High Voltage Engineering, Burlington, Mass.)

P. Stynes (Now teaching physics, Winthrop High School, Winthrop, Mass.)

Degrees Granted:

H. Wilhelmsen, S.B., Electrical Engineering, September 1968

P. Stynes, S.B., Electrical Engineering, September 1968

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

Research Report

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

1.0 Electron Ionization Cross Sections

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

Sponsorship: Air Force Materials Laboratory

A program concerning the measurement of electron-impact ionization cross sections using a large quadrupole mass spectrometer is continuing. Studies have now been made on the single and double ionization of monatomic silver, copper and lead. A large group of calibration experiments has also been completed, though further experiments will be necessary. Improvements have been made in the collimation of the ionizing electron beam, and new feedback stabilization circuitry has been installed and tested. An atomic beam shutter, thermally driven by a small bimetallic strip, has been installed above the ionization chamber to permit better control in weight-gain measurements. The shutter operates in a fraction of a second, and is not affected by variations in ambient temperature.

Currently an intensive effort is being made to obtain cross sections for carbon. These measurements are more difficult, first because of the higher temperatures required to vaporize carbon, and second, because carbon tends to evaporate as a mixture of trimers, monomers, and dimers. To facilitate these measurements a motor driven neutral beam chopper has been installed, a high-temperature water-cooled Knudsen cell has been constructed, and a window for making optical pyrometer measurements of cell temperature has been installed.

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.

2.0 Ion Implantation of Semi-Conductor Devices

Personnel: F. G. Ruedenauer, M. D. Brody, C. K. Crawford

Sponsorship: NASA Electronics Research Center, Lincoln Laboratory

A project designing ion sources suitable for both high and low energy ion implantation is continuing. Gas sources have been designed and tested which provide microampere currents at high brightness and good gas

efficiency. Currently high temperature sources which can produce useful quantities of ions from high temperature elements are under construction. The sources are being designed to require a minimum of heating power. Thus they are small in size and carefully heat shielded.

A project to use ions from the plasma produced by the impact of a laser beam on a solid has been tentatively discontinued. It appears that this method cannot compete at present due to the cost of the laser required, and problems with plasma confinement. These problems may relax in the future.

3.0 Electron and Ion Beam Testing of Microcircuitry

Personnel: C. K. Crawford

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 into 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.

Theses:

- P. Stynes, "A High Current Density Electron Gun," S.B. Thesis, Department of Electrical Engineering, August 1968.
- H. Wilhelmsen, "A Molecular Beam Source for Bismuth," S.B. Thesis, Department of Electrical Engineering, August 1968.

Publications:

- C. K. Crawford, "Mass Spectrometer Ion Source for Ionization Cross Section Measurement," J. Vacuum Science and Technology 5, 131 (1968).
- C. K. Crawford, "Comments on 'Duoplasmatron Ion Beam Source for Vacuum Sputtering of Thin Films'," The Review of Scientific Instruments 39, 1390 (1968).
- C. K. Crawford, "The Microcanonical Ensemble and Small Systems," Bulletin Am. Phys. Soc. 13, 952 (1968).
- C. K. Crawford, "Design of Thermal Manipulators for Ultra-high Vacuum," J. Vacuum Science and Technology 5, 37 (1968).
- C. K. Crawford, "Electron Microbeam Testing of Integrated Circuits," Particle Optics Laboratory Technical Report #2, MIT, February 1968; 29 pages, 8 figures.
- C. K. Crawford and K. L. Wang, "Electron-Impact Ionization Cross Sections for Silver," J. Chem. Phys. 47, 4667 (1967).

METALLURGY AND MATERIALS SCIENCE

I. PHYSICS OF SOLIDS

(All personnel from Department of Metallurgy and Materials Science except where indicated)

Faculty:

B. L. Averbach, Professor
R. 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 Science and Engineering

Graduate Students:

J. Ahn, IBM Fellow
P. Benquey, FMFA Fellow and Research Assistant
G. R. Caskey, Research Assistant
W. K. Choo, Research Assistant
R. Currat, Research Assistant
W. S. Ewing, NSF Trainee
J. W. Franz, Research Assistant
I. S. Goldstein, Research Assistant
D. Hall, NSF Trainee
S. Lee, Research Assistant
K. R. Morash, NSF Trainee
T. A. Postol, NSF Trainee
M. D. Rechtin, Research Assistant
R. Shemanski, NSF Trainee
D. J. Silversmith, Research Assistant
P. J. Tobin, International Nickel Fellow
J. Zagarins, Research Assistant

Support Staff:

G. Pishenin, Engineering Assistant

Frances M. Gedziun, Secretary

Anne W. Howe, Secretary

Personnel who have left:

S. C. Moss, Associate Professor (on Sabbatical leave at the University of Melbourne, Australia)

J. Ahn, IBM Fellow (Now at IBM, E. Fishkill Facility, Hopewell Junction, New York)

P. Benquey, FMFA Fellow (Now French Army, Maisonsal Fort, France)

D. Hall, NSF Trainee (Now U.S. Army, Watertown, Massachusetts)

P. J. Tobin, International Nickel Fellow (Now Department of Physics, University of Arizona, Tucson, Arizona)

Degrees Granted:

J. Ahn, Ph.D., Metallurgy, August 1968

J. F. Graczyk, Ph.D., Metallurgy, June 1968

P. J. Tobin, Ph.D., Metallurgy, August 1968

P. Benquey, M.S., Metallurgy, August 1968

Sponsorship:

The research listed here has been sponsored by the following agencies. Specific sponsorship is listed under the individual research report.

Office of Naval Research, Nonr-1841(48), DSR 78954; Nonr-1841(35), DSR 77618; Nonr-1841(17), DSR 70172

National Science Foundation, NSF GP-5463, DSR 76275; GK-1947, DSR70847

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

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

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

United States Steel Corporation, DSR 70216

Xerox Corporation, DSR 74997

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

Research Report

The object of much of the research in the Physics of Solids group is the development of a quantitative understanding of some of the more complex forms of condensed matter. For example, electron states are studied in binary alloy systems as opposed to the simpler pure materials, and the structures and properties of liquids, amorphous materials, and alloys are studied in addition to 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; and the study of local environments in solids. Research programs in these areas are described in detail in the following sections.

1. Spin Correlations in Magnetic Materials

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

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

The arrangement of spins in ferromagnetic and antiferromagnetic materials is being investigated by means of neutron scattering observations. Work here has shown that there is considerable short range order above the critical temperature and the local arrangement of spins is being investigated at temperatures above and below the magnetic transition. Detailed studies have been made in single crystals of MnO and NiO, and work on CoO is now underway. It appears that short range antiferromagnetic order in these materials exists well above the critical

temperature, and the situation is complicated by the presence of both magnetic twin and spin domains. These spin waves change as the critical temperature is approached and the development of long range order from these modulated structures is being investigated.

Spin correlations are also being measured in permanent magnet materials. The magnetic properties of these materials are being measured, and attempts are being made to correlate the magnetic parameters with the spin arrangements.

2. Atomic Arrangements in Selenium

Personnel: Professors Roy Kaplow, B. L. Averbach

Sponsorship: Xerox Corporation, DSR 74997

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 these are corrected by means of an iterative computer method.

Attempts are being made to match the experimental amorphous distribution functions with models which involve perturbations of the atom positions in the crystalline forms of selenium and the corresponding selenium-arsenic alloys. A computer array consisting of 100 atom positions is used and perturbations are chosen by a Monte Carlo procedure which allows only those perturbations which improve the fit to the experimental distribution function. It has been shown that relatively small static displacements are sufficient to convert the crystalline structures to the observed vitreous form.

The Monte Carlo simulation of the amorphous

structure is being improved and these techniques are being applied to the study of other vitreous materials.

3. Quantum Oscillatory Phenomena in Lead and Dilute Lead-Indium Alloys

Personnel: Professors D. J. Sellmyer, B. L. Averbach and P. J. Tobin

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

Quantum oscillations in the transverse magnetoresistance of high purity lead have been observed at temperatures of 1.2°K and magnetic field strengths up to 150 kilogauss. Measurements of the angular dependence of the observed frequencies in a (111) plane agree with existing de Haas-Van Alphen results for the third zone Fermi surface, in regions where these two sets of data overlap. The absence of magnetic breakdown in fields up to 150 kilogauss has been established, and the observed oscillations are therefore not due to an oscillatory probability for magnetic breakdown, but are true Shubnikov-de Haas oscillations.

In addition to oscillatory terms attributable to the third zone Fermi surface, a frequency lower than any previously reported for Pb has been detected. It has not been possible to dismiss this as due to a crystal imperfection, and it is noteworthy that the data are consistent with the requirements of a fourth zone Fermi surface piece according to the nearly-free electron model.

De Haas-van Alphen studies have been carried out on pure Pb and Pb-In alloys having concentrations up to 0.62 atomic percent. Attention has been directed to the details of the arms of the third zone Fermi surface.

For concentrations greater than 0.13 atomic percent a new frequency is detected, the appearance of which is attributed to the non-extremal nature of one of the orbits on the third zone arm in pure Pb. The observed decrease in the size of the third zone arm as the conduction electron concentration decreases can be satisfactorily accounted for by rigid band theory.

4. Quantum Oscillatory Phenomena in Dilute Beryllium-Copper Alloys

Personnel: Professor D. J. Sellmyer, B. L. Averbach;
I. S. Goldstein

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

Measurements are being made of the changes in Fermi surface and electron scattering in beryllium alloyed with small amounts of copper. Cross-sectional areas, cyclotron masses, and scattering temperature are being measured with the de Haas-van Alphen and Shubnikov-de Haas effects in fields up to 150 kG. In addition, attention is being directed to the effect of alloying upon magnetic breakdown which occurs in the basal plane in beryllium.

5. Fermi Surface of AuSb_2

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

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

High-field magnetoresistance and quantum oscillatory phenomena have been investigated in the metallic compound AuSb_2 in fields up to 150 kG.

The high-field magnetoresistance results

indicate that AuSb_2 is a compensated metal and its Fermi surface supports open orbits in $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ directions. The field dependence of the magnetoresistance indicates that these open orbits are lost in the highest fields as a result of magnetic breakdown.

De Haas-van Alphen and magnetoresistance oscillations were investigated in $\{100\}$ and $\{110\}$ planes with DC and field-modulation techniques. The orientation dependence of eight sets of extremal Fermi surface areas was determined. Where the frequency and cyclotron mass data for the two experiments overlapped, the agreement was excellent. However, some anomalies in the field dependence of the oscillatory amplitude in certain field directions were found and these appear to result from magnetic breakdown.

A nearly-free-electron Fermi surface model was constructed assuming that the contribution of each gold and antimony atom to the conduction bands is one and five electrons, respectively. This model has topological properties which are consistent with the observed open orbit directions. However, it was shown that the model is incapable of explaining the angular dependence of the measured extremal areas. On this basis, it is concluded that the nearly-free-electron model does not represent, even approximately, the Fermi surface of AuSb_2 .

6. Fermi Surface of AuAl_2 , AuGa_2 , and AuIn_2

Personnel: Professor D. J. Sellmyer (in cooperation with J. T. Longo and P. A. Schroeder of Michigan State University)

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

Measurements of the magnetoresistance and Hall voltage have been made in the high field region ($\omega_c \gg 1$) on the metallic fluorite compounds AuAl_2 , AuGa_2 , and AuIn_2 . The results have been compared with those expected from the nearly-free-electron (NFE) model. These compounds are uncompensated. Hall effect measurements for $\underline{B}$ in $\langle 100 \rangle$ and $\langle 111 \rangle$ indicate significant departures of the real Fermi surface from the NFE model. The magnetoresistance measurements in principal planes and directions, with one exception, support the NFE model, but the dimensions of the two-dimensional areas of aperiodic open orbits show pronounced deviations. A proposed empirical model gives considerable improvement with both Hall effect, magnetoresistance, and de Haas-Van Alphen measurements. In the best AuGa_2 crystal, whiskers have been observed and classified in some detail. The magnetoresistance has been calculated for $\underline{B}$ in $\langle 100 \rangle$ assuming a constant relaxation time and a model of the fourth electron zone with a topography similar to the NFE Fermi surface.

7. Transport Properties and Magnetism in Alloys

Personnel: Professor D. J. Sellmyer; G. R. Caskey,
J. W. Franz

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

The general nature of the electronic structure and magnetic impurity states was investigated in β' FeAl, CoAl and NiAl alloys. These alloys have the CsCl structure at the equiatomic composition. Measurements of the electrical resistivity, thermoelectric power, and magnetoresistance were made between 1.4°K and 296°K. The major results of the investigation are as follows: (1) The

magnitude of the resistivity and sign of the thermopower in the sequence NiAl, CoAl, FeAl appear to indicate a lowering of the Fermi surface from a position above to a position within the transition metal d-bands as one goes from NiAl to FeAl. (2) The change in sign of the magnetoresistance between 4.2°K and 2.97°K in FeAl alloys near the equiatomic composition is consistent with a paramagnetic to antiferromagnetic transition deduced from earlier susceptibility measurements in this system. (3) An anomaly at about 53 percent nickel in a Nordheim-Gorter thermopower analysis may be taken as further evidence for the Fermi surface-Brillouin zone interaction inferred from previous optical reflectance measurements for the NiAl system.

(4) With regard to impurity states in these alloys, there was a negative magnetoresistance at 4.2°K in all three alloys for concentrations of more than about 50 percent transition metal. In addition there was a resistance minimum at about 30°K for CoAl alloys in 50.4 to 51.5 percent cobalt and an anomalous low temperature thermopower for these same alloys. These phenomena seem to result from localized impurity states that possess or nearly possess a magnetic moment. The impurity states are associated with transition metal atoms on aluminum sites and thus have eight nearest neighbor transition metal atoms. The behavior in the CoAl system has several of the hallmarks of the Kondo effect but localized spin fluctuations and multiple spin complexes cannot be ruled out.

8. Thermoelectricity in Dilute Magnetic Alloys

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

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

An experimental investigation of the thermoelectric power and other transport properties of dilute magnetic alloys has been initiated. The presence of localized moments in metallic alloys leads to an anomalously large electron scattering cross-section which, in turn, gives rise to giant thermopowers. Alloys of small amounts of transition metals in noble metals will be studied to understand the spin-flip scattering processes as well as effects associated with interactions of the impurity atoms with each other.

9. Theoretical Electronic Structure of Polyatomic and Macro-Molecules

Personnel: Professor K. H. Johnson

Sponsorship: None

A Green's function technique has been developed for the approximate calculation of the molecular orbitals of complex polyatomic and macro-molecules. The computational simplicity and applicability of this method to molecules of arbitrary stereochemical structure are dependent on the adoption of a model Hartree-Fock Hamiltonian similar to that used in solid-state theory. The method is of particular advantage in treating polyatomic systems where more conventional molecular orbital techniques are difficult to implement. Applications are currently being made to sulfur and chlorine oxy-anions. Projected applications will include the metal porphyrins and helical macromolecular systems such as DNA, which are important to biology.

10. Theory of Impurity and Surface States

Personnel: Professor K. H. Johnson

Sponsorship: None

A new theoretical model, based on Green's function formalism, has been developed for determining localized impurity and surface electronic states and their effects on the band structure, density of states, and Fermi surface of the host crystal. The model has the advantage over other methods that one can treat multiple impurities forming clusters, lines, and planes in the crystal, as well as 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 potentials is a valid first approximation. Vacancies are also within the scope of the model. A study of the relationship between this approach and the electronic theory of non-dilute disordered alloys is also being made.

11. Theoretical Energy Bands and Fermi Surfaces of Alloys

Personnel: Professor K. H. Johnson

Sponsorship: Advanced Research Projects Agency, SD-90,
DSR 78892

The Green's function method is being used to determine from first quantum principles the electronic energy bands and Fermi surfaces of alloys. Computer programs permit the direct computation of Fermi surface cross sections using a constant energy search of the Brillouin zone, as well as the calculation of band profiles with a constant wave-vector search. The programs also

allow the direct determination of relativistic and magnetically spin-polarized bands, and are applicable to crystals with several atoms per unit cell. Applications are currently being made to ordered intermetallic compounds for which reliable experimental Fermi surface and optical data are available. Work has been completed on the compounds β' -CuZn, β' -AgZn, β' -AuZn, and β' -NiAl. An extension of the Green's function approach, in conjunction with statistical methods, is being made to disordered solid-solution alloys, with a first-order treatment of alpha brass having been completed.

12. The Structure of Liquids

Personnel: Professors Roy Kaplow, B. L. Averbach;
Sang C. Lee, Alan Renninger

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

The three-dimensional arrangements of atoms in liquids are being carried out in terms of perturbations of simpler structures, such as the crystalline form or models involving particular molecular units. Computer programs which were developed earlier and applied to amorphous selenium, have been refined. These programs walk atoms from a pre-set arrangement (in three dimensions) to new configurations which are consistent with experimental pair-distribution functions. The programs are now sufficiently efficient to be applied to high density liquid metals. Various statistical parameters can be extracted from the final arrangement, such as:

(a) displacements from original sites, (b) distortions of pair-distances as a function of pair separation,

(c) distribution of bond angles, (d) three-atom (and higher order) correlation functions. Programs have been written, in addition, which plot arbitrary two-dimensional sections of the final arrangement, the atoms being indicated as circles of the (hard-ball) size, as intersected by the plane. Some initial results have been obtained for liquid lead with the initial model being perfectly crystalline apart from the random removal of sufficient atoms to reduce the average density to that of the liquid. Although this work is still in progress, we will mention three qualitative results: (a) Reasonably close fits to the pair distribution function have been attained without achieving major redistribution of the vacancy volumes; (b) While the nearest neighbor, three-atom, included bond angles remain peaked about the normal (crystalline) angles, broadening of the peaks is sufficiently great that virtually all angles are present which are larger than the minimum imposed by the distance of closest approach; (c) A number of instances have been seen, in the two-dimensional sections, of atoms all or partially between two adjacent neighbors, i.e., along the diffusion path to a vacancy. Such motion has been discussed earlier, in connection with the question of melting.

This research program also includes computational work regarding interaction potentials in liquids and the experimental measurement of distribution functions and of low angle scattering.

13. Compton Scattering

Personnel: Professor Roy Kaplow; Roland Currat

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

We are measuring the energy distribution of X-rays, which have suffered inelastic scattering in single crystals of beryllium, as a function of the scattering direction in the crystal. These data may be interpreted in terms of the true momentum distribution of electrons in the crystal.

The experimental arrangement now utilizes a large target source, a flat LiF analyzing crystal and two Soller slits for collimation. Data have been obtained for several crystallographic directions and the apparatus is now being devoted to long duration runs in order to achieve improved statistical precision.

Recent efforts have been concentrated on various factors which enter into the initial reduction of the data. Consideration has been given to eliminating subsidiary wavelengths passed by the analyzing crystal, the variation of the reflectivity of the analyzing crystal, the separation of the contributions from each of the $K\alpha_1$ and $K\alpha_2$ components in the incident beam, and the unfolding of instrumental broadening.

14. "Mossbauer Effect in Iron Alloys"

Personnel: Professor Roy Kaplow; W. K. Choo (in cooperation with Professor Morris Cohen)

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

This research concerns the measurement of Mossbauer spectra in alloys of iron with (primarily) interstitial type elements, particularly carbon. Specimens are being produced by splat-quenching, which allows

formation, at suitable compositions, of unusual phases, as well as an inhibition of diffusion controlled rearrangements which may occur, in ordinary quenching, during the formation and cooling of well known phases. Much of our recent efforts have been devoted to experimental refinements, aimed at achieving specimens of improved uniformity and long duration Mössbauer absorption runs of sufficient stability; high statistical precision and good resolution is required simply to identify the many resonance peaks from certain alloys, which contain three or more well defined ferromagnetic and paramagnetic phases, and whose spectra contain evidence of an even larger variety of iron-atom sites. Initial data has been obtained for a few iron-carbon alloys containing 0.9 to 2.8 wt. % carbon, and an iron-boron alloy. These results indicate that in addition to providing access to certain physically important interaction parameters pertaining to those sites which give rise to identifiable resonances (e.g., the isomer, electric quadrupole, and magnetic hyperfine interactions), the Mössbauer spectra appear to allow identification that is more definite than, or at least complementary to X-ray diffraction with alloys containing a number of different and imperfect structures.

Our current work is concerned with

(a) providing a more detailed characterization of the structures produced by rapid cooling, (b) resolving questions about the rearrangement of carbon atoms during the cooling of martensite formed above and below room temperature, (c) deducing, from the hyperfine interactions, the electronic alterations suffered by iron atoms in identifiable environments.

15. On-Line Systems for Numerical Analysis

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

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

A new version of MAP is presently being implemented. A language processor has been written, using the AED facilities. It will allow the new system to include, in the familiar equation-like format, multi-parameter operators, conditional choices, a much enlarged group of data types, and one- two- and three-dimensional functions. Present work is concentrated on the structuring of and programming for the data base and operator tables.

16. The Structure of SiO

Personnel: Professor Roy Kaplow; John Yasaitis

Sponsorship: Advanced Research Projects Agency, SD-90
DSR 78892

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.

17. Alterations in Near-Neighbor Configurations
Due to Cold Work in Nickel

Personnel: Professor Roy Kaplow; Patrick Benquey

Sponsorship: Advanced Research Projects Agency, SD-90,
DSR 78892

Utilizing a complete Fourier Transform analysis of X-ray diffraction data, it has been possible to obtain the radial atomic pair distribution function in polycrystalline nickel, in the annealed and cold-worked

condition at room temperature (300°K) and 80°K . In these results it is possible to see, directly, the actual distribution of the displacements between atoms for each of the nominal near neighbor separations (bond distances). The atomic displacements in these experiments are caused by thermal vibrations and (in the cold-worked dislocations). While the results have not yet been fully analyzed, it appears that the major effects may be interpreted in terms of average interaction energy considerations, without direct reference to models for the structure of defects.

18. Low Angle Scattering of X-Rays

Personnel: Professors S. C. Moss, J. Cahn; J. Kitler
Sponsorship: Advanced Research Projects Agency, SD-90,
DSR 75125

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

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

19. Scanning Electron Diffraction and Electron Energy Losses in Thin Films

Personnel: Professor S. C. Moss; Dr. J. F. Graczyk;
T. A. Postol
Sponsorship: Advanced Research Projects Agency, SD-90,
DSR 75125

A scanning electron diffraction attachment with energy analysis has been constructed for use in conjunction with a J.E.M.6AS electron microscope. This attachment permits the direct recording of diffracted electron

intensities as a function of angle with an accuracy of $\pm 0.1\%$. The attachment can be operated so as to exclude all but the elastically diffracted electrons, or, alternatively, to detect electrons with a measureable amount of energy loss.

The effect of inelastic scattering has been investigated in the diffraction patterns of aluminum and gold films. At low values of the scattering vector where the inelastic background is very intense its removal reveals diffraction effects which otherwise would have been invisible.

Plasmon losses have been measured in Al and found to occur at 14.9 eV. The effect of alloying on the plasma energy has been investigated for alloys of Al-Zn in the composition range up to 10% atomic Zn. The loss spectra are found to be similar to the Al spectrum and show a detectable decrease in the plasmon energy with increasing Zn concentration.

Theses

J. F. Graczyk, "Selected Studies in Scanning Electron Diffraction", Ph.D., Department of Metallurgy, June, 1968.

J. Ahn, "De Haas-van Alphen Effect, High-Field Magnetoresistance, and the Fermi Surface of AuSb_2 ", Ph.D., Department of Metallurgy, August, 1968.

P. J. Tobin, "Quantum Oscillatory Phenomena in Lead and Dilute Lead-Indium Alloys", Ph.D., Department of Metallurgy, August 1968.

P. Benquey, "Radial Distribution Function in Annealed and Cold-Worked Nickel", M.S., Department of Metallurgy, August, 1968.

Publications

Averbach, B. L., Atomic Aspects of Fracture Propagation, Presented at the International Conference on the Strength of Metals and Alloys, Tokyo, Japan (September 4-8, 1967).

Moss, S. C. and Averbach, B. L., Local Atomic Configurations in a Gold-Nickel Alloy, Small-Angle Scattering, Gordon and Breech, New York, 335-350 (1967).

Woodilla, J. E., Jr. and Averbach, B. L., Modulated Structures in the Au-Ni Alloys, Acta Met. 16, 255-263 (1968).

Kaplow, Roy, Rowe, T. A. and Averbach, B. L., Atomic Arrangement in Vitreous Selenium, Phys. Rev. 168, No. 3 (April, 1968), pp. 1068-1079.

Averbach, B. L., Trapping Models of Photoconductors, Comments on Solid State Phys. 1, 1-4 (1968).

Strong, S. L. and Kaplow, Roy, The Structure of Crystalline B_2O_3 , Acta Cryst. B24, Part 8 (1968), pp. 1032-1036.

Clapp, P. C. and Moss, S. C., Correlation Functions of Disordered Binary Alloys - II, Phys. Rev. 171, No. 3 (1968), pp. 754-763.

Moss, S. C. and Clapp, P. C., Correlation Functions of Disordered Binary Alloys - III, Phys. Rev. 171, No. 3 (1968), pp. 764-777.

Gangulee, A. and Moss, S. C., Long Range Order in Ag_3Mg , Jnl. of Appl. Cryst. 1, Part 2 (1968), pp. 61-67.

- Longo, J. T., Schroeder, P. A. and Sellmyer, D. J.,
Topology of the Fermi Surface of AuAl_2 , Phys. Letters
25A, 747 (1967).
- Amar, H., Johnson, K. H. and Sommers, C. B., Electronic
Structure of Alpha Brass, Phys. Rev. 153, 655 (1967).
- Johnson, K. H., Multiple-Scattering (Green's Function) Model
for Polyatomic Molecules II, Intern. Jnl. Quantum Chem.
1S, 361 (1967).
- Johnson, K. H., Extension of the Korringa-Kohn-Rostoker
Method to the Impurity Problem, Phys. Letters 27A,
138 (1968).

Papers Accepted for Publication

- Averbach, B. L. and Pearson, P. K., Properties and
Performance of 52100 Bearing Steels, Trans. Quarterly.
- Woodilla, J. E., Jr. and Averbach, B. L., Moiré Patterns
in Electron Transmission Through Gold-Nickel Alloys,
Acta Met.
- Averbach, B. L., Propagation of Fracture in Polycrystalline
Beryllium, 2nd Inter. Conference on Fracture, England.
- Averbach, B. L., Spinodal Instability in Some Solid
Solutions, Comments on Solid State Phys.
- Mozar, B., Keating, D. T., and Moss, S. C., Neutron
Measurement of Clustering in the Alloy CuNi.
- Jones, K., Moss, S. C., and Rose, R. M., The Effect of
Small Oxygen Additions on the Elastic Constants and
Low Temperature Ultrasonic Attenuation of Nb Single
Crystals, Acta Met.
- Caskey, G. R. and Sellmyer, D. J., Local Moment Formation
and Resistivity Minima in CoAl Alloys, Jl. Appl. Phys.

Goldstein, I. S., Tobin, P. J., and Sellmyer, D. J., Low-Pass Superconducting Filter for Use in High Magnetic Fields, Rev. Sci. Instr.

Johnson, K. H., The Energy Bands and Fermi Surfaces of IB-IIB Alloys, in Status of Energy Band Theories of Metals and Alloys (Gordon and Breach Science Publishers, Inc., New York).

Johnson, K. H., Scattering Model for the Bound Electronic States of an Impurity Complex in a Crystal, Inter. Jl. Quantum Chem.

Johnson, K. H. and Connolly, J. W. D., On Calculating the Localized Electronic States of Surface and Line Defects, Phys. Letters.

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:

A. J. Gregor, Technical Instructor

Graduate Students:

J. W. Pugh, Part-time Instructor
A. W. Sherman, Part-time Instructor
G. T. Eldis, NASA Trainee
F. B. Fletcher, Research Assistant
D. S. Gelles, NSF Trainee
M. K. Koul, Research Assistant
D. B. Snow, Research Assistant
R. Stevenson, Research Assistant

Support Staff:

Miriam E. Yoffa, Engineering Assistant
R. Goss, Technician
J. Operacz, Technician
Marguerite A. Meyer, Secretary

Personnel who have left:

H. H. Johnson, Visiting Professor (Returned to the Department of Materials Science, Cornell University, Ithaca, New York)
Dr. F. S. Gardner, Visiting Scientist (Returned to the Office of Naval Research, Boston, Massachusetts)
H. J. Rack, Research Assistant (Now at Lockheed-Georgia Company, Marietta, Georgia)
R. C. Whittemore, Engineering Assistant (Retired)
E. D. Sudenfield, Technician (Now at Magnet Laboratory, MIT)

SECTION C - METALLURGY AND MATERIALS SCIENCE

155

Degrees Granted:

M. K. Koul, Ph.D., Metallurgy, September 1968 (Now DSR Staff, MIT)
H. J. Rack, Sc.D., Metallurgy, June 1968

Sponsorship:

The research is sponsored by the following agencies. Specific sponsorship is also listed under each individual report.

Advanced Research Projects Agency, Contract No. SD-90, DSR 75128
Bethlehem Steel Corporation, DSR 70391
Office of Naval Research, Contract No. Nonr-1841(35), DSR 77618
United States Steel Corporation, DSR 70216
Vasco Metals Corporation, 21990
National Science Foundation Fellowship
NASA Traineeship
Air Force Materials Laboratory, Contract AF 33(615)-3866, DSR 76337

Research Report

1.0 Strain-Enhanced Diffusion

Personnel: Professor M. Cohen

Sponsorship: None

Further attention is being given to the mechanism of strain-enhanced diffusion in metals during plastic deformation. Vacancy-controlled processes have been ruled out as the predominant mechanism in this phenomenon. The most satisfactory model thusfar involves the diffusion of metal atoms along the core of moving dislocations. There is an analogy here with the diffusion of interstitial atoms through the lattice, suggesting the need for studies of interstitial diffusion during plastic deformation.

2.0 Nucleation of Martensitic Transformations

Personnel: Professor M. Cohen; M. K. Korenko

Sponsorship: Office of Naval Research

Isothermal nucleation of the martensitic transformation in iron-nickel-manganese alloys is being examined further to establish the nature of the pre-existing embryos or preferred nucleation sites. Current results indicate that such singularities are normally too few in number to be encountered by transmission electron microscopy. Accordingly, the number of nucleation sites in the parent phase is being varied by plastic deformation, with measurements of nucleation kinetics

and electron microscopy then being applied. Special attention is being given to the role of carbon as an impurity in influencing the nucleation rates. Some of the anomalies observed may result from this source.

3.0 Mössbauer Investigations of Iron-Base Interstitial Phases

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

Sponsorship: Office of Naval Research

Splat-quenched iron-carbon martensites are being investigated by Mössbauer measurements to determine the local environment of the interstitial atoms. These results suggest that the carbon atoms are positively charged in both martensite and austenite, whereas interstitial nitrogen atoms are negatively charged. However, this interpretation is clouded by the possibility of carbon redistribution at room temperature (aging) prior to the measurements. In order to forestall this complication, the splat-quenched specimens are being subcooled immediately in liquid nitrogen and the measurements carried out before warming back to room temperature.

4.0 Splat-Quenching of Iron-Base Alloys

Personnel: Professor M. Cohen, in collaboration with Professor M. C. Flemings; F. Fletcher

Sponsorship: Office of Naval Research; United States Steel Corporation

It was previously shown, that a new iron-carbon solid solution based on hexagonal close-packed iron can be retained by splat quenching. The unit cell corresponds to Fe_{12}C_3 , but the actual carbon content is usually less than this composition. This phase is stabilized by the presence of silicon, and its nature is being studied by Mössbauer spectroscopy. However, extremely rapid cooling rates are necessary even in the presence of silicon, and therefore attempts to produce this phase in bulk quantities (even with the hammer-and-anvil type of splat quenching) have not proved successful up to now.

5.0 Strain Hardening at Very High Strains

Personnel: Professor M. Cohen; A. M. Sherman

Sponsorship: Office of Naval Research

A model has been developed for the strain hardening of metals at very high degrees of plastic deformation (wire drawing), involving the formation and refinement of subgrains. The strengthening is found to increase in inverse proportion to the cell size, and the model accounts

for this relationship. The extent of strain hardening, then, is controlled by the cellular-refinement process and this, in turn, is opposed by dynamic-recovery processes. Hence, the efficiency of strain hardening by this mechanism depends on the inhibition of dynamic recovery. Such possibilities are being investigated in an attempt to achieve ultrahigh-strength levels. In addition, comparisons are being made among body-centered cubic, face-centered cubic, and hexagonal close-packed phases.

5.0 Strengthening Mechanisms

Personnel: Professor M. Cohen; G. T. Eldis, A. M. Sherman, F. Fletcher

Sponsorship: Office of Naval Research; Bethlehem Steel Corporation

It has been established that the ausform-strengthening of iron-nickel-carbon martensites can be explained by an increase in dislocation density and the carbon-pinning of these dislocations. The next step in this program is to determine the role of carbide-forming elements, on the grounds that carbide precipitation may contribute further to the enhanced strengthening. To this end, chromium and molybdenum have been added to a series of iron-nickel-carbon alloys, and the ausform-strengthening characteristics are being studied. These alloys have transformation temperatures below the ambient, thus making it possible to test virgin martensites both in the regular and ausformed conditions.

Experiments are also underway to check the order-disorder theory of tetragonal versus cubic iron-carbon martensites. It is possible that the validity of this hypothesis is being obscured by carbon depletion during quenching or aging, and special alloy compositions are being prepared to avoid such extraneous effects. Conceivably, some of the discrepancies to date have resulted from substructural differences in the martensite: i. e., dislocations versus internal twins.

Martensitic steels are known to have a higher flow stress in compression than in tension, this being the so-called strength-differential effect. The nature of this phenomenon is being examined. Special attention is being given to a theory which depends on the existence of non-linear elastic displacements of the iron atoms next to carbon atoms in the martensitic lattice.

6.0 Transformation and Deformation Studies in Titanium Alloys

Personnel: Professor J. F. Breedis; M. K. Koul

Sponsorship: Air Force Materials Laboratory

The mechanical properties of beta-isomorphous titanium alloys and

their related deformation and transformation structures have been studied in detail. The deformation structures investigated include dislocation arrangements, twinning, and stress-induced martensite developed during shock deformation and at normal rates of straining. Omega-phase formation, phase separation and martensitic transformations are also being examined in these alloys.

Examination of martensite in titanium-molybdenum alloys shows that the two kinds of martensite with $\{334\} \beta$ and $\{344\} \beta$ habit planes form in low molybdenum and high molybdenum alloys, respectively. Further, $\{334\} \beta$ - type martensite contains essentially no internal structure whereas $\{344\} \beta$ - type martensite contains dislocations and stacking faults.

Study of the omega-phase in titanium-vanadium alloys has verified that the omega-phase is hexagonal in structure with an axial ratio of 0.61 and an orientation relationship given by: $(111)\beta // (0001)\omega$ and $[1\bar{1}0]\beta // [11\bar{2}0]\omega$. The omega-phase forms by a diffusion-controlled nucleation and growth process on quenching and aging. It was shown that the omega-phase is not a transition phase. The equilibrium alpha-phase develops on aging, not from the omega-phase but at the beta-omega interface and grows to consume the omega-phase. The effect of omega-phase on the tensile properties of a titanium-vanadium alloys was determined.

Thermodynamic calculations, using the regular solution approximation, showed a positive heat of mixing for titanium-vanadium and titanium-niobium alloys while a negative value was obtained for titanium-molybdenum. Thus, a tendency for phase separation in the vanadium and niobium alloys and a tendency for ordering in molybdenum case is indicated. On this basis, the stability of the beta-phase and the phase diagrams in these systems were rationalized. Experimental investigation of phase separation by spinodal decomposition in various alloys did not prove conclusive but such a tendency is indicated for titanium-niobium alloys.

Stress-induced martensite in titanium-vanadium alloys was conclusively shown to be hexagonal close-packed in structure and not twinned body-centered cubic or tetragonal as recently proposed.

Twinning was observed in body-centered cubic titanium - 22 weight percent vanadium after straining at room temperature. Precipitation of a fine dispersion of the omega-phase completely suppressed twinning. The dislocation substructure of twinned specimens contained straight screw dislocations whereas in the latter case, dislocation tangles were observed.

The effect of shock deformation on the structure and tensile properties of titanium and titanium-molybdenum alloys was also studied. It was found that unalloyed titanium (hexagonal close-packed) showed the greatest relative increase in strength whereas titanium - 26 weight percent molybdenum (body-centered cubic) showed the least. The maximum ultimate tensile strength is developed in titanium - 12.5 weight percent molybdenum. A phase transformation: $\alpha(\text{h. c. p.}) \rightarrow \beta(\text{b. c. c.}) \rightarrow \alpha'$ (martensite), was observed in unalloyed titanium shock deformed at 200 kilobars pressure. In both unalloyed titanium and titanium - 12.5 weight percent molybdenum, the enhanced strength values were attributed to simultaneous occurrence of phase transformation and deformation during passage of the shock wave.

7.0 Strengthening by Spinodal Decomposition

Personnel: Professor J. F. Breedis; D. S. Gelles

Sponsorship: National Science Foundation Fellowship; Air Force
Materials Laboratory

A program to determine the effect of a spinodally decomposed structure on strength properties in metals has been initiated. Employing Meijering's ternary regular solution model for miscibility gap formation (Phillips Research Reports, 1950 and 1951) and heat of mixing data of Kaufman and Bernstein (AFML reports, 1967), the Ti-Nb-Ru system is found to be worthy of study. The development of the spinodally decomposed structure will be examined through diffraction techniques and transmission electron microscopy, and correlated with observed yielding and work hardening behavior.

8.0 Deformation of Hexagonal Close-Packed Alloys

Personnel: Professor J. F. Breedis; D. B. Snow

Sponsorship: Advanced Research Projects Agency

The objective of this investigation is to elucidate the deformation behavior of a 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. The principal variables of interest in the program are composition, and temperature and strain-rate of testing. The operating slip systems and associated dislocation arrangements are being determined. A reliable method for the preparation of foils to be studied in transmission in the electron microscope has been developed. Attempts are presently being made to obtain single crystals of the alloys using the floating-zone technique.

9.0 Fatigue of Titanium Alloys

Personnel: Professor J. F. Breedis; R. Stevenson

Sponsorship: Advanced Research Projects Agency

It has been demonstrated that the number of cycles necessary to produce failure at a given stress in titanium increases with decreasing grain size. To investigate the role played in fatigue by dislocation substructure, as distinct from fatigue crack propagation, commercial and high-purity titanium and titanium alloys are being studied as functions of constant strain amplitude and grain size in the push-pull mode. In particular, the influence of grain size upon the saturation stress, the number of cycles required to achieve saturation, and the development of the defect structure with cyclic straining are being studied. A push-pull device having good axiality of loading has been incorporated into a conventional mechanical testing machine. This device is capable of studying the development of hysteresis loops in a range of strain amplitudes extending from a few percent to the microstrain (less than 10^{-3}) region. Observation of the dislocation structure has shown that a well-developed cell structure develops close to saturation. Preliminary results indicate that saturation occurs after fewer cycles in finer-grained commercial-purity titanium.

Publications:

- S. R. Pati and Morris Cohen, "Nucleation of the Isothermal Martensitic Transformation," accepted for publication in *Acta Metallurgica*.
- R. C. Ruhl and Morris Cohen, "Splat Quenching of Iron-Carbon Alloys," accepted for publication in *Transactions of The Metallurgical Society of AIME*.
- R. C. Ruhl and Morris Cohen, "Splat Quenching of Iron-Nickel-Boron Alloys," accepted for publication in *Transactions of The Metallurgical Society of AIME*.
- D. A. Karlyn, J. W. Cahn and Morris Cohen, "The Massive Transformation in Copper-Zinc Alloys," accepted for publication in *Transactions of The Metallurgical Society of AIME*.
- J. F. Breedis, A. Lawley, "Structural Aspects of Fatigue in Single Crystal Beryllium," *Metal Science Journal*, in press.
- M. K. Koul, J. F. Breedis, "Strengthening of Titanium Alloys by Shock Deformation," *Proceedings, The International Conference on Titanium*, London, England (1968).
- I. R. Sprung, J. F. Breedis, "Martensitic Transformations in Iron-Ruthenium," to be published.

III. PHYSICAL METALLURGY - Thermodynamics of Metallic Systems;
Properties of Solid Solutions; Deformation and Annealing;
Radiation Damage

(All personnel from Department of Metallurgy and Materials Science)

Faculty:

M. B. Bever, Professor

Research Staff:

A. K. Jena, DSR Staff

Graduate Students:

R. O. Scattergood, Research Assistant (to August 1968)

J. W. Pugh, Research Assistant (from June 1968)

Support Staff:

L. I. Sudenfield, Project Technician

Theresa R. Walsh, Secretary

Personnel who have left:

R. O. Scattergood, Research Assistant (to Argonne National Laboratory,
Argonne, Illinois)

Degrees Granted:

R. O. Scattergood, Sc.D., Metallurgy, September 1968

Sponsorship:

This research was sponsored by the agencies listed below. Specific sponsorship is also stated under each individual report.

Office of Naval Research, Nonr 3963(19), DSR 74675

U. S. Atomic Energy Commission, AT(30-1)-1002, DSR 76831
(through August 31, 1968)

National Aeronautics and Space Administration, Grant NsG-496,
DSR 74569 (through May 31, 1968)

Research Report

This research was concerned with the thermodynamics of metallic systems, the properties of solid solutions, the deformation and annealing of metals and alloys and the effects of radiation on electronic materials. The experimental techniques used included liquid metal solution calorimetry, electrical measurements, X-ray diffraction and mechanical tests.

1.0 Thermodynamics of Metallic Systems

1.1 The Temperature Dependence of the Heat of Formation of the Compound AgMg

Personnel: M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research

Metal solution calorimetry can be used to measure heats of formation at various temperatures including temperatures below room temperature. In this investigation, heats of formation at 78⁰, 195⁰ and 273⁰K of the compound AgMg containing 50.1 at. % Mg were measured. The temperature coefficient of the heat of formation is negative and appreciable near 78⁰K, but with increasing temperature it decreases gradually to a small value near room temperature. This behavior of the temperature dependence of the heat of formation is consistent with the reported high-temperature heat contents of AgMg, Ag and Mg and can be explained by contributions of lattice heat capacities.

1.2 Enthalpy Interaction Coefficients of Silver, Cadmium and Gold in Dilute Quaternary Tin-Rich Solutions

Personnel: M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research

Equations for the heat effects of additions of mixtures of multi-component phases to a solution were derived in terms of the enthalpy interaction coefficients. By these equations and the measured composition dependence of the heat effects on addition of mixtures of silver-cadmium solid solutions and elemental gold to liquid tin-rich solutions, values of

the enthalpy interaction coefficients η_{Ag}^{Ag} , η_{Cd}^{Cd} , η_{Au}^{Au} , η_{Ag}^{Cd} , η_{Ag}^{Au} , and η_{Cd}^{Au} in tin-rich solutions at 541°K were obtained. Analysis of these results in terms of the regular solution theory and the quasichemical theory suggested that near the melting point of the solvent, association in the solution becomes important.

1.3 The Heats of Formation of Silver-Rich Silver-Cadmium Solid Solutions

Personnel: M. B. Bever; J. Waldman; A. K. Jena

Sponsorship: Office of Naval Research and Atomic Energy Commission

The heats of formation at 273°K of six silver-rich silver-cadmium solid solutions and the heat of formation at 78°K of one solid solution were measured by tin solution calorimetry. The heats of formation were analyzed in terms of the quasichemical theory. If the enthalpy difference between a hypothetical f. c. c. form and the h. c. p. form of cadmium was taken into account, this analysis did not support the conclusion put forth in the literature that electronic effects make significant contributions to the heats of formation of silver-rich silver-cadmium solid solutions. The temperature dependence of the heats of formation was appreciable and negative near 78°K, but decreased gradually to nearly zero above 400°K. The relative partial enthalpies per gram-atom of silver at 541°K and cadmium at 532° and 541°K in tin were also determined.

1.4 Dilute Solutions of Gold in Bismuth-Tin Alloys

Personnel: M. B. Bever; J. H. Smith; A. K. Jena

Sponsorship: Atomic Energy Commission, Office of Naval Research

The relative partial gram-atomic enthalpy of gold at infinite dilution in bismuth, tin and six bismuth-tin alloys was measured at 623°K. Values of the composition dependence of the relative partial enthalpy were measured in bismuth and two bismuth-tin alloys at 623°K; the temperature coefficients of the relative partial enthalpy in three bismuth-tin alloys were also determined. An analysis based on the quasichemical theory shows that non-zero values of the relative energy of solute-solute bonds $\Delta \epsilon_{ii}$ and the variation of the coordination number Z can explain the behavior of the

dilute solutions of gold in bismuth-tin alloys.

1.5 Thermodynamics of Phases in the System Gold-Tin

Personnel: M. B. Bever; A. K. Jena

Sponsorship: Office of Naval Research

Calorimetric and X-ray measurements on metastable phases of gold-tin alloys prepared by splat cooling are continuing in collaboration with Professor N. J. Grant and Dr. B. C. Giessen. The investigation of thermodynamic properties of related stable gold-tin phases at low temperatures is also continuing.

2.0 Properties of Solid Solutions

2.1 Short-Range Order in Copper-Rich Copper-Aluminum Alloys

Personnel: M. B. Bever; R. O. Scattergood

Sponsorship: Atomic Energy Commission

The short-range order in copper-aluminum alloys containing nominally 6, 11, and 15 atomic percent aluminum was investigated by X-ray diffraction measurements. Single crystals of the three compositions were shown to have short-range order. Quenching from various annealing temperatures reduced the degree of order. Measurements of the resistance as a function of the annealing temperature prior to quenching and of the quenching rate were made to explore the short-range order in quenched specimens.

3.0 Deformation and Annealing

3.1 Effects of Short-Range Order on the Deformation of Copper-Rich Copper-Aluminum Alloys

Personnel: M. B. Bever; R. O. Scattergood

Sponsorship: Atomic Energy Commission

The investigation mentioned in 2.1 was extended to the effects of short-range order on the deformation of copper-aluminum alloys. Microhardness tests and tensile tests were carried out to determine the effects of annealing and quenching treatments on the deformation behavior. A correlation was found between changes in the short-range order and initial yielding; this was characterized by a yield drop which depended on the degree of order. The flow stress was independent of changes in the short-range order resulting from different annealing and quenching treatments.

An analysis suggests that the yield drop is controlled by the stress required to reduce the short-range order. Yielding terminates when the order-independent flow stress mechanism takes over. This mechanism appears to be a type of uniform lattice friction, rather than the effect of distributed point obstacles. The destruction of short-range order continues during the remainder of the deformation, but has no effect on the flow stress.

3.2 The Annealing Behavior of Cold Worked AgMg

Personnel: M. B. Bever; A. K. Jena

Sponsorship: Atomic Energy Commission

The investigation of the annealing behavior of cold worked specimens of the intermetallic compound AgMg has been concluded. The resistometric and calorimetric results have been supplemented by X-ray results by Dr. J. H. Westbrook of the Research and Development Center, General Electric Co., Schenectady, New York.

After cold work to small torsional strains at several temperatures, single recovery stages were observed in a specimen of the compound AgMg containing 50.1 at. % Mg and in a specimen containing 44.2 at. % Mg. In all cases, hyperbolic rate laws were obeyed. The recovery process in the 50.5% Mg composition is interpreted as due to the restoration of order and dislocation annealing; the recovery process in the 44.2% Mg composition is interpreted as vacancy promoted ordering; in this composition appreciable thermal disordering was also observed.

4.0 Radiation Damage of Electronic Materials

Personnel: M. B. Bever; A. Gangulee

Sponsorship: National Aeronautics and Space Administration

The irradiation of specimens of $\text{Bi}_2\text{Te}_2\text{Se}$ with 7.5 MeV protons to a maximum integrated dose of 2×10^{16} protons/cm² and their examination by X-ray diffraction were completed in an earlier period. Work on the interpretation of the results is continuing.

Publications:

- A. Gangulee and M. B. Bever, "The Silver-Rich Solid Solutions in the System Silver-Magnesium: I. Short-Range Order," *Trans. Met. Soc. AIME*, 242, pp. 272-277 (1968).
- A. Gangulee and M. B. Bever, "The Silver-Rich Solid Solutions in the System Silver-Magnesium: II. Long-Range Order," *Trans. Met. Soc. AIME*, 242, pp. 278-283 (1968).
- A. M. Reti, A. K. Jena, and M. B. Bever, "On the Solid Solutions of Tin Telluride and Lead Telluride," *Trans. Met. Soc. AIME*, 242, pp. 371-373 (1968).
- J. H. Smith and M. B. Bever, "Effects of Cold Work on the Stored Energy, Electrical Resistivity and Tensile Properties of Gold," *Trans. Met. Soc. AIME*, 242, pp. 880-884 (1968).
- A. K. Jena and M. B. Bever, "The Heat of Formation of the Compound AuSb_2 and the Partial Enthalpies and Enthalpy Interaction Coefficients of Antimony and Gold in Liquid Tin," *Trans. Met. Soc. AIME*, 242, pp. 1453-1454 (1968).
- A. K. Jena, B. C. Giessen, M. B. Bever, and N. J. Grant, "The Metastability of Gold-Antimony Phases Prepared by Splat Cooling," *Acta Met.*, 16, pp. 1047-1051 (1968).
- A. Gangulee and S. C. Moss, "Long-Range Order in Ag_3Mg ," *J. Appl. Cryst.*, 1, p. 61 (1968).
- A. K. Jena and M. B. Bever, "On the Temperature Dependence of the Heat of Formation of the Compound AgMg ," *Trans. Met. Soc. AIME* (in press).
- P. Beardmore and M. B. Bever, "The Annealing Behavior of a Gold-Silver Alloy after Deformation at Low Temperatures," *Trans. Met. Soc. AIME* (in press).
- G. Bartsch, "Neutronenbeugungsuntersuchungen an Cu-Ni-Zn-Legierungen", accepted for publication in *Zeitschrift für Metallkunde*.
- A. K. Jena and M. B. Bever, "Enthalpy Interaction Coefficients of Silver, Cadmium and Gold in Dilute Quaternary Tin-Rich Solutions," accepted for publication in *Trans. Met. Soc. AIME*.
- J. Waldman, A. K. Jena and M. B. Bever, "The Heats of Formation of Silver-Rich Silver-Cadmium Solid Solutions," accepted for publication in *Trans. Met. Soc. AIME*.

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, Metallurgy and Materials Science
K. C. Russell, Assistant Professor

Graduate Students:

J. Goldman, Part-time Instructor
J. Baker, NSF Trainee and Part-time Instructor
S. Bhattacharyya, Research Assistant
C. Biswas, Research Assistant
P. Boswell, Research Assistant
R. Heady, Research Assistant
J. Johnson, Research Assistant
J. Kitler, Research Assistant
J. Morral, Research Assistant
M. Richards, Research Assistant
J. Wells, Research Assistant

Support Staff:

W. Carrasco, Technician
A. Santangelo, Technician
Martha Finta, Secretary

Personnel who have left:

J. Sandor, Research Assistant (Now with Professors Gatos and Witt)
W. Carrasco, Technician (Now with Northeastern University)

Sponsorship:

The research is sponsored by the following agencies. Specific sponsorship is also listed under each individual report.

National Institutes of Health, Contract No. DE02384-03, DSR 70952
National Science Foundation, Contract No. GK-1304, DSR 70236
National Science Foundation Fellowship

Advanced Research Projects Agency, Contract No. SD-90, DSR 75129
Office of Naval Research, Nonr-3963(07), DSR 79809
Sloan Fellowship, DSR 27695

Research Report

1.0 Theory of Spinodal Decomposition

Personnel: J. W. Cahn; J. E. Morral

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 of particular interest to us and we believe analysis of the rate of resistivity decay during annealing will provide information 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 $50\text{ \AA}$ to 1μ 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 $100 - 1000\text{ \AA}$.

4.0 Nucleation Involving Condensed Phases

Personnel: J. W. Cahn, K. C. Russell; J. Baker, S. Bhattacharyya, C. Biswas, P. Boswell, J. Goldman, R. Heady, J. Johnson, M. Richards

Sponsorship: National Science Foundation

This is a broad theoretical and experimental investigation of the thermodynamics and kinetics of nucleation in condensed phases.

It has been postulated that splat-cooling extends the terminal solid solubility by quenching the melt below the extrapolated $\alpha/\alpha + \text{L}$ boundary to where the single-phase α is more stable than $\text{L} + \alpha$. Mr. Baker has shown this to be incorrect by obtaining extended solubility at the zinc end of the cadmium-zinc system which shows retrograde solubility. Mr. Baker has further shown that the usual assumption of interface equilibrium is not valid in this system and in fact one component is

increasing its chemical potential upon solidification.

Mr. Heady has completed an analysis of the forces involved in liquid phase sintering of spheres, showing that the usual forces balance obtained intuitively is indeed very close to the exact solution. Mr. Heady is condensed systems where all ancillary data on thermodynamics and surface tension are known.

We have cooperated with Dr. D. Hoffman of Ford Scientific Laboratory in extending the Gibbs-Wulff construction to determining the equilibrium form of a particle at a grain boundary of arbitrary orientation. Also with Dr. Hoffman we have reformulated the equations of capillarity in solids.

We have found the standard treatments of precipitate coarsening to be inadequate on two points: allowance is made neither for the effect of volume fraction precipitate on coarsening rate nor for fluctuations in the numbers of atoms impinging on the precipitate particle. Mr. Bhattacharyya is making a careful test of the theory by measuring coarsening rates of γ -iron particles in a copper matrix.

We have presented a theoretical analysis of frequency factors and incubation times for the nucleation of second-phase particles on grain boundaries. Mr. Biswas is investigating grain boundary precipitation of cobalt from a copper-cobalt solution to test the theory.

We have analyzed the coherency strains for compositional inhomogeneities in elastically anisotropic crystals. These strains affect the free energy and lead to a new term in the diffusion equation for coherent processes. Anisotropy tends to stabilize either simple cubic or $\langle 111 \rangle$ arrays of particles, depending on the elastically soft directions.

5.0 Phase Separation and Crystallization in Glass

Personnel: J. W. Cahn; J. Kitler

Sponsorship: Advanced Research Projects Agency

The Kratky low-angle X-ray camera is presently being used to study phase separation in the BaO-SiO₂ 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.

Theses:

- J. E. Morral, "Stability of Ternary Alloys to Continuous Changes of Phase", Ph.D. Thesis, Department of Metallurgy and Materials Science, September 1968.

Publications:

- J. W. Cahn, "Coherency Stress in Elastically Anisotropic Crystals and Its Effect on Diffusional Processes", Proceedings of an International Symposium on Phase Transformations in Crystalline Solids, Sidney Press, Limited, Bedford, England, p. 1 (1968).
- J. W. Cahn, "The Metastable Liquidus and Its Effect on the Crystallization of Glass", The Journal of the American Ceramic Society, In press.
- J. C. Baker and J. W. Cahn, "Solute Trapping by Rapid Solidification", Acta Met., in press.
- D. A. Karlyn, J. W. Cahn, and M. Cohen, "The Massive Transformation in Copper-Zinc Alloys, TMS-AIME, in press.
- K. C. Russell, "Linked-Flux Analysis of Nucleation in Condensed Phases," Acta Met. 16, 761 (1968).
- 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 ", submitted to Physics of Fluids.
- D. B. Dawson, E. J. Willson, P. G. Hill, and K. C. Russell, "Nucleation of Supersaturated Vapors in Nozzles, Part II: C_6H_6 , $CHCl_3$, CCl_3F , and C_2H_5OH ," submitted to Physics of Fluids.
- K. C. Russell, "Nucleation on Gaseous Ions", accepted by J. Chem. Phys.
- K. C. Russell, "Comment on Nucleation and Coarsening in Binary Condensed Systems", submitted to J. Colloid Interface Science.
- K. C. Russell, "Nucleation in Solids", in Phase Transformations, ASM, Metals Park, Ohio, in press.
- K. C. Russell, "Grain Boundary Nucleation Kinetics", submitted to Acta Met.

V. HIGH TEMPERATURE METALLURGY

Faculty:

N. J. Grant, Professor, Metallurgy and Materials Science

Research Staff:

Dr. B. C. Giessen, Research Associate, Metallurgy and Materials Science

Dr. Rong Wang, Research Associate, Metallurgy and Materials Science

Graduate Students:

P. Bridenbaugh, Research Assistant, Metallurgy and Materials Science

G. Campbell, Graduate Fellow, Metallurgy and Materials Science

W. T. Compton, Research Assistant, Metallurgy and Materials Science

H. Dalal, Research Assistant, Metallurgy and Materials Science

R. Davison, Graduate Fellow, Metallurgy and Materials Science

K. Erhardt, Research Assistant, Metallurgy and Materials Science

G. Ewell, Research Assistant, Metallurgy and Materials Science

F. Hunkeler, Research Assistant, Metallurgy and Materials Science

C. Jansen, Research Assistant, Metallurgy and Materials Science

R. Kane, Research Assistant, Metallurgy and Materials Science

D. Kenagy, Research Assistant, Metallurgy and Materials Science

M. Lebo, Research Assistant, Metallurgy and Materials Science

R. Ray, Research Assistant, Metallurgy and Materials Science

V. Sarin, Research Assistant, Metallurgy and Materials Science

W. Schilling, Research Assistant, Metallurgy and Materials Science

W. F. Smith, Research Assistant, Metallurgy and Materials Science

L. van Swam, Research Assistant, Metallurgy and Materials Science

A. Wilson, Research Assistant, Metallurgy and Materials Science

S. Wolf, Research Assistant, Metallurgy and Materials Science

Support Staff:

G. Kiessler, Engineering Assistant, Metallurgy and Materials Science

U. Erhardt, Engineering Assistant, Metallurgy and Materials Science

Lydia White, Secretary, Metallurgy and Materials Science

Personnel who have left:

B. C. Giessen (to Chemistry Dept., Northeastern University, Boston)

J. T. Blucher (to Industrial Materials Technology, Cambridge, Mass.)
H. Matyja (Returned to University, Warsaw, Poland)
Rong Wang (to Dept. of Materials Science, USC, Los Angeles, Calif.)
P. Knudsen (to Danish Atomic Energy Estab., Roskilde, Denmark)
P. Bridenbaugh (to Alcoa Research Lab., New Kensington, Pa.)
G. Ewell (Ames Research Lab., U. S. Army, Moffett Field, Calif.)
F. Hunkeler (to Howmet, Muskegon, Michigan)
R. Kane (to International Nickel Research Lab., Suffern, New York)
D. Kenagy (to Alcoa Research Lab., New Kensington, Pa.)
W. F. Smith (to Florida Technological Univ., Orlando, Florida)

Degrees Granted:

P. Bridenbaugh, Sc. D., Metallurgy and Materials Science, Sept. 1968
G. Ewell, Sc. D., Metallurgy and Materials Science, June 1968
F. Hunkeler, Sc. D., Metallurgy and Materials Science, June 1968
R. Kane, Sc. D., Metallurgy and Materials Science, June 1968
D. Kenagy, Met. E., Metallurgy and Materials Science, June 1968
W. F. Smith, Sc. D., Metallurgy and Materials Science, June 1968

Sponsorship:

Aeronautical Systems Division, Wright-Patterson AFB, F33615-67-C1441,
DSR 70324
National Aeronautics and Space Administration, NsG-117-61, DSR 76243
Naval Air Systems Command, Dept. of the Navy, N00019-67-C-0500
DSR 70569
International Copper Research Association, DSR 70925
National Science Foundation, GK-1374, DSR 70290
U. S. Army Res. Office, Durham, DA31-124-ARO-D-328, DSR 74613
Office of Naval Research, Nonr 3963(18) DSR 74621

Research Report

1.0 Dispersion Strengthening

Personnel: N. J. Grant; F. Hunkeler, H. Dalal, W. Schilling, G. Ewell,
D. Kenagy, S. Wolf, M. Singh.

Sponsorship: NASA, ONR

Initially this laboratory was concerned with oxide dispersed alloys;

now the effort is being extended to intermetallic and other hard phases, such as TiC, Ni_3Al , etc. There are differences in bonding energies, low temperature strength, high temperature strength and alloy stability at high temperatures among these classes of dispersion strengthened alloys. Support comes from several groups.

Mr. Hunkeler, working with Fe-BeO alloys, has demonstrated that the flat slopes of curves of log stress vs. log rupture time plots are due to very short, jagged grain boundary segments which are pinned by oxide particles, preventing grain boundary sliding and migration. Recrystallization of these high extrusion ratio alloys leads to decreased creep resistance. Cold working clearly results in higher strength values. Excellent properties are reported from 1000 to 1400 degrees F, superior to those of both commercial ferritic and austenitic stainless steels and high alloy steels.

Mr. Dalal has shown excellent stability of ThO_2 particles in an 80 Ni-20Cr base composition at temperatures to 2400 degrees F. The role of chromium and Cr_2O_3 on alloy stability and on ThO_2 stability is being determined.

Mr. Schilling has produced some of the highest strength copper alloys ($\text{Cu-Al-Al}_2\text{O}_3$) ever reported, utilizing surface plus internal oxidation of Cu-Al powders. Excellent room temperature strength as well as superior stress rupture properties at 450 to 850 degrees C are reported. The alloys are oxidation resistant and stable even after long term exposure at 1000 degrees C.

Mr. Ewell found that coarse slip bands do not form in oxide dispersed alloys, and that fine slip is often difficult to observe and forms only after 5% strain or more. Fractures at high temperatures are intercrystalline with short crack segments forming randomly and then coupling to form the fracture.

Mr. Kenagy using five types of dispersoids (oxide, metallic and intermetallic) at 3 volume fractions (3 to 11%), and at 3 sizes for each dispersoid (from 0.01 to 25 microns diameter), has proved that the metallic and intermetallic dispersoids result in strengthening through bonding, whereas the oxide dispersoids do not lead to strengthening but do promote structure stability by pinning grain and subgrain boundaries.

Mr. Singh has initiated studies of BeO dispersed nickel and nickel-base alloys. The high melting point, the high free energy of formation of the oxide and its lack of reactivity make BeO an ideal dispersoid. Internal and surface oxidation are planned; extensive solid solution strengthening will be utilized to achieve much higher levels of strength at the lower temperatures.

Mr. Wolf is measuring energy release calorimetrically for a number of these alloys, placing particular emphasis on Fe-BeO alloys, which can be prepared both by alpha and gamma extrusion (with stored energy of cold work and without), and Cu-Al-Al₂O₃ alloys.

2.0 Equilibrium and Non-Equilibrium Alloy Phase Studies

Personnel: N. J. Grant; B. C. Giessen, Rong Wang, C. Jansen, R. Ray, V. Sarin.

Sponsorship: U. S. Army Research Office-Durham; NSF; NASA; International Copper Research Association

Rapid quenching of liquid metals and alloys (splat cooling) has been responsible for achieving cooling rates as high as 10^9 degrees C sec⁻¹. These high cooling rates yield some unusual structures (and presumably properties). Large changes in solute solubility, in grain size and dendrite size, formation of metastable intermetallic phases, formation of amorphous and microcrystalline phases are a few of the observed changes. In addition to enhancement of alloy theory, research is also slanted toward production of bar stock to permit evaluation of these highly modified structures.

Dr. Wang has studied a wide range of pseudobinary AB₃ phases based on combinations of gold with transition metals. A number of metastable compounds have been reported as well as large shifts in solubility limits.

Dr. Giessen has examined presumed amorphous phases for evidence of microcrystallinity and has shown that some of these structures may indeed be microcrystalline, involving as few as 50 to 75 atoms per crystal. A computer program relating crystal size, structure and the resultant diffraction pattern shows good agreement.

Mrs. Jansen has measured increases in solubility in alloys of aluminum containing Cu, Pd, Fe, Co, Mn, Ni, and reports large increases in all cases. Cu is soluble to 18 at. pct. (vs. about 5.5 at the eutectic); Fe is soluble to about 4 at. pct. (vs. less than 0.05 at room temperature). The decomposition of these supersaturated solutions is now under way and may lead to some interesting speculation regarding alloying theory. The system Al-Cu will be studied in detail for aging behavior, leading to tests, if possible, of mechanical properties.

Mr. Ray is examining Ni and Fe base metals alloyed with other transition metals. These are high temperature potential alloys and as such offer interesting alloy systems for commercial exploitation. The inter-

metallics in these alloys are being examined, supersaturation is being recorded, and decomposition of metastable structures is being followed.

Mr. Sarin is studying rapidly quenched copper alloys containing Cr, Zr, Mg and combinations these to observe changes in solubility due to quenching. Formation of fine dendritic structures is being followed with the expectation that such structures will result in alloys of improved strength and high temperature stability.

3.0 The Role of Strain Rate, Strain, and Temperature in Low Strain Rate, High Strain Fatigue

Personnel: N. J. Grant; J. T. Blucher, K. Erhardt

Sponsorship: Aeronautical Systems Division, Wright-Patterson AFB

Dr. Blucher has extended the low cycle fatigue studies on high purity aluminum down to strain rates of $0.25\% \text{ min}^{-1}$ and up to $500\% \text{ min}^{-1}$. These tests were performed at 80 to 500 degrees F and clearly show important strain rate effects even at room temperature for total strain amplitudes of 2%.

Mr. Erhardt, utilizing the scanning electron microscope in stereo, at the Center for Materials Science and Engineering, has been studying the fracture of aluminum alloy 2024 in the T4 temper. Fractures are initiated at large inclusions and second phase particles (which are often cracked prior to the start of the test) or on slip bands. Some cracking occurs by decohesion between the matrix and the intermetallic phase. Many fine cracks are formed at various levels relative to the major advancing crack. These crack levels are finally interconnected by serrated fatigue cracks climbing walls which may approach 90 degrees. Serration fatigue cracks are much more extensive and at numerous levels and in many more directions during crack growth than has previously been indicated.

4.0 Development of Chromium Base Alloys

Personnel: N. J. Grant; R. Davison, A. Wilson L. van Swam

Sponsorship: Naval Air Systems Command and Fairchild Camera and Instrument Company Fellowship

Chromium alloys offer one of the last remaining chances for oxi-

dation resistant, high temperature alloys. Protection against nitrogen embrittlement, lowering of the transition temperature for brittle fracture, and increasing the strength both at low and high temperatures are the aims of this program.

Mr. Davison has prepared alloys of chromium containing finely dispersed carbides by powder metallurgy techniques to avoid contamination usually associated with melting techniques, and in an effort to keep the carbides fine and well dispersed. A measure of success has been achieved in that transition temperatures for brittle fracture have been kept as low as 250 degrees C. Refinements in processing are currently under way.

Mr. Wilson has produced a series of Cr-Ru-Ti alloys by melting, followed by crushing to a coarse powder, followed by sheath extrusion. The ruthenium tends to lower the transition temperature for brittle fracture; the titanium series both as a second phase former (Cr_2Ti) and as a getter or barrier against nitrogen pick-up. The combination of properties in early tests looks promising. Resistance to nitrogen solution at 1800 and 2000 degrees F in 100 hours is fair; low temperature properties are excellent, and stress rupture data for 1800 and 2000 degrees F are very good.

Mr. v. Swam is studying Cr-Ru- ThO_2 alloys. The Cr-Ru alloys are melted and attrited to near-micron powder, to which ThO_2 is added. Extrusions will be made to provide test material to compare against the Cr-Ru alloys of Mr. Wilson (above) which utilize a second phase which is an intermetallic rather than an oxide. This work is in its early stages.

5.0 Deformation and Fracture at Hot Working Temperatures

Personnel: N. J. Grant; R. Kane, P. Bridenbaugh, W. T. Compton, G. Campbell

Sponsorship: Naval Air Systems Command and Forging Industry Educational and Research Foundation Fellowship

Utilizing cast ingot structures, Mr. Kane has shown that bcc iron is softer and more ductile than fcc iron. He has also shown that for a single phase material hot plasticity increases with increasing temperature and strain rate. Of great interest, he has demonstrated that coarse grained, cast, ingot structures can be grain refined by a series of strain steps (10 to 20% strain per step) at high strain rates and high temperatures. Time (in minutes) is necessary between each strain step (isothermal) to permit recrystallization to a new finer grain size. Too small a strain leads usually to grain coarsening.

Mr. Bridenbaugh ran parallel studies with pure Mo and a highly alloyed TZC composition. For the pure single phase Mo, high strain rates and high temperatures yield the highest plasticity, although the strain rate effect is small. For the 3-phase TZC alloy slow strain rates and high temperatures yield the highest plasticity. Step-strain grain refinement does not occur with pure Mo because the system recovers too readily from the imposed high strain rate cold work effect.

Mr. Campbell has initiated studies of hot plasticity for an 18-8 stainless steel. In addition to measuring the hot plasticity, the recrystallization of this alloy will be studied in detail as a function of the amount of strain, strain rate, temperature and holding time after straining.

Mr. Compton is pursuing parallel studies with an Fe-W-C alloy. In addition to determining the hot plasticity as a function of strain rate and temperature, step-strain response will be studied, and mechanical properties of the resultant superfine grained structures will be determined.

6.0 Aging in Al-Zn-Mg Alloys

Personnel: N. J. Grant; W. F. Smith

Sponsorship: None

Mr. Smith has determined the role of solution temperature and aging temperature on the resultant aging pattern, with special concern for grain boundary depletion. The effects of small Cu, Ag and Cr additions to these Al-Mg-Zn alloys for control of boundary depletion were determined. A mechanism for the depletion process is proposed. Both mechanical properties and stress corrosion cracking were studied in terms of boundary depletion.

Theses:

P. Bridenbaugh, "Deformation of Molybdenum and Molybdenum Alloys at High Strain Rates and High Temperatures", Sc. D. Thesis, Department of Metallurgy and Materials Science, September 1968.

G. Ewell, "The Deformation and Fracture of Dispersion Strengthened Alloys", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1968.

F. Hunkeler, "Oxide Dispersion Strengthened Iron-Beryllia Alloys", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1968.

R. Kane, "Deformation of Iron at High Temperatures and High Strain

Rates", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1968.

W. F. Smith, "Aging Behavior in Aluminum-Zinc-Magnesium Alloys", Sc. D. Thesis, Department of Metallurgy and Materials Science, June 1968.

Publications:

R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "New Microcrystalline Phases in the Nb-Ni and Ta-Ni Systems", *Acta Met.* 15, 1693, November 1967.

L. L. J. Chin and N. J. Grant, "Release of Stored Energy in Oxide Dispersion Strengthened Copper", *Powder Metallurgy*, 10, 344, 1967.

R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "Metastable Hexagonal Close-Packed Phases in Ni-Rich Ni-Nb and Ni-Ta Alloys", *J. Less Comm. Met.* 13, 611, 1967.

B. C. Giessen, U. Wolff, and N. J. Grant, "Metastable Simple Cubic Phases Based on Sb and Bi", *Trans. Met. Soc. AIME*, 242, 597, 1968.

B. C. Giessen, U. Wolff, and N. J. Grant, "The Metastable System Ga-Al and the Atomic Volume at Twelfefold Coordinated Ga", *Jour. Appl. Crystallography*, 1, 30, 1968.

V. Sadagopan, B. C. Giessen, and N. J. Grant, "Crystal Chemistry of Au-Rich Binary Alloy Phases with Heavy Rare Earths", *Jour. Less Common Metals*, 14, 279, 1968.

C. Borromee-Gautier, B. C. Giessen, and N. J. Grant, "Metastable Phases in the Pb-Sb and Pb-Bi Systems", *Jour. of Chem. Physics*, 48, 1905, March 1968.

R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "Metastable bcc Phases in the V-Ni and Ni-In Systems", *Materials Science and Engineering*, 2, 314, 1967-68.

J. T. Blucher, Per Knudsen, and N. J. Grant, "Effect of Strain Rate and Temperature at High Strains on Fatigue Behavior of SAP Alloys", *Trans. AIME Met. Soc.*, 242, 1605, 1968.

R. Ray, B. C. Giessen, and N. J. Grant, "New Non-Crystalline Phases in Splat Cooled Transition Metal Alloys", *Scripta Metallurgica*, 2, 357, 1968.

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
H. Sakao, Visiting Scientist
T. Engh, Visiting Scientist
M. Onillon, Research Associate

Graduate Students:

A. Briskine, Research Fellow
C. W. Finn, Research Fellow
T. K. Kuwabara, Graduate Fellow
F. Larche, Research Assistant
M. Maulvault, Graduate Fellow
J. Nichols, Graduate Fellow
H. Piolet, Graduate Fellow
J. Popper, Graduate Fellow
G. K. Sigworth, Graduate Fellow
P. A. Tichauer, Research Fellow
P. J. Yavorsky, Research Fellow

Support Staff:

J. Stack, Technician
Virginia Stevens, Secretary
Diane R. Mountain, Secretary

Personnel who have left:

S. Ban-ya (Returned to Tohoku University, Sendai, Japan)
W. B. Eisen (Now at Crucible Steel Co., Pittsburgh, Pa.)
J. Sodi (Now at Iberioamerican University, Mexico City)
J. Yarwood (Now at Olin Mathieson Co., New Haven, Conn.)

Sponsorship:

American Iron and Steel Institute, Contract Numbers 15A, 15B, 15C,
194, 195, DSR 71115-6-7-8, 71120
American Iron and Steel Institute, Contract 164, DSR 70542
American Iron and Steel Institute, Contract 146, DSR 70544
National Bureau of Standards, CST-280, DSR 76360
National Science Foundation, GK-754, DSR 70821
United States Army, DAHC 04-67-C-0036, DSR 70368
Carbon Products Division, UCC, DSR 71299
International Nickel Co. Fellowship
National Defense and Education Act Fellowship
Fuji Iron & Steel Co. Ltd., Japan Fellowship
French Government Fellowship

Research Reports1.0 Physico-Chemical Properties of Sulfides

Sponsorship: American Iron and Steel Institute, and National Science Foundation

Mr. Nichols is beginning a study of the interfacial tension between the liquid oxysulfides of iron and γ or δ iron. The experimental methods to be employed are the sessile drop method and grooving of the grain boundary of the metal in contact with the sulfide.

Mr. Sodi completed his study of the electrochemical and thermodynamic properties of some of the sulfides of refractory metals. He measured the free energies of formation of Hf_2S_3 , MoS_2 , Nb_2S , NbS , Ta_2S , TaS , ThS_2 , WS_2 and Zr_3S_2 using an emf cell with CaCl_2 as the electrolyte. He also measured the effect of temperature and sulfur pressure on the conductivity of BaS , CaS , HfS_2 and SmS_2 . His results indicate that these sulfides show n-type conduction as a result of metal interstitials.

2.0 Problems of Heat and Mass Transfer

Sponsorship: American Iron and Steel Institute, Carbon Products Division, UCC

Mr. Sigworth is studying the factors that determine the rate at which particles of solid iron, and of Fe-Al and Fe-Si alloys dissolve in liquid iron.

He is measuring the solution rate with controlled conditions of flow in the liquid metal.

Mr. Piolet is investigating the possible convective motion of the interdendritic liquid in a partially solidified ingot as a result of density differences because of composition and temperature differences. Currently he is working with an aluminum alloy containing 4.5% Cu. Later he will work with steels.

Professor Engh from the Technical University at Trondheim, Norway, is visiting our Department for a year. He and Professor Elliott have underway an extensive study of the heat transport processes in grate-sintering and pelletizing. Professor Engh is also analyzing the dynamic character of closed-circuit comminution circuits.

Mr. Maulvault is proceeding with measurements of the heat flow patterns in the electroslog remelting process. He is making measurements of the temperatures in a small operating system and is comparing them with predictions obtained from a theoretical model. It is intended to relate the conditions of heat flow to ingot structure.

Mr. Popper is using the same basic theoretical model employed by Mr. Maulvault to predict the temperature distribution in the hearth refractories of a blast furnace. The purpose of the work is to improve on the analyses in the literature in which relatively simple analytical solutions to the differential equations have been employed.

The study of the heat flow and temperature conditions in the electrode of an electric-arc furnace is being continued. Mr. Yavorsky has just shown that the assumption of axial symmetry is satisfactory for the case of an electrode in the presence of two others. He is proceeding with an analysis of the electrode on the chemical processes in the furnace during steelmaking.

3.0 Inclusions in Steels

Sponsorship: American Iron and Steel Institute

The study of the influence of metal composition, temperature and cooling rate on the composition and morphology of the oxysulfide inclusions observed in Fe-O-S alloys has been completed by Mr. Yarwood. He showed that the observed structures in the solidified samples can be explained in terms of an "isolation" model. The model assumes that small droplets of the non-metallic liquid are isolated from the metallic liquid by the solid metal dendrites that form during the solidification process. The sulfur content of the droplets formed late in solidification are high in sulfur. This

work is supervised jointly by Professors Flemings and Elliott.

Mr. Kuwabara is developing an experimental method by which it should be possible to determine quite precisely the fraction liquid of a partially solidified steel sample just prior to it being quenched to room temperature. He is using the method in the study of the effect of an inclusion formation of additions of sulfur to liquid steel before and after deoxidation.

4.0 Structure of Liquid Complex Oxides

Sponsorship: American Iron and Steel Institute

Mr. Finnis is studying the structure of phosphate melts containing up to 10 mol. pct. SiO_2 . Quenched glasses are dissolved in water and the phosphate ion chain length analyzed by paper chromatography. It has been demonstrated that shorter phosphate chains, which do not contain any silicate, are found in the silicophosphates than in the binary phosphates. Silicon presumably enters the phosphate chains at the center and hydrolysis, on solution, produces the break-up of the chains.

5.0 Electrochemical Processes in Steelmaking

Sponsorship: American Iron and Steel Institute

Mr. Tichauer is studying kinetic processes at iron and inert electrodes in calcium aluminate melts. Of particular interest are the reactions involving sulphur and oxygen, which occur in, for example, electroslog remelting. A high temperature cell, with liquid electrodes, has been constructed and transient measurements are made, using the galvanostatic method.

6.0 Thermodynamic Properties of Alloy Systems

Sponsorship: U.S. Army and American Iron and Steel Institute

The study of the effect of temperature and carbon content on the activity of carbon in Fe-C was completed by Professor Ban-ya before he returned to Japan. Drs. Onillon and Rosof are measuring the effect of the usual alloying elements on the carbon content of austenite saturated with graphite.

The measurements of the activity of silicon in α and γ iron and in

Ag-Si alloys will be completed by Dr. Sakao before he returns to Japan in February. In this work he has employed a novel emf cell that uses a silica-saturated $\text{Li}_2\text{O-SiO}_2$ electrolyte.

Publications:

- T. Kuwabara and J. F. Elliott, "Distribution Ratios in Ternary Alloys," Trans., TMS-AIME (in press).
- T. A. Engh and J. F. Elliott, "Temperature Profiles due to Combustion with Heat Exchange Between a Gas Stream and a Bed of Granular Solids," Proceedings "IX Session De Communications Scientifiques", Bucarest, Roumania, January 1969.
- S. Ban-ya, J. F. Elliott and J. Chipman, "Activity of Carbon in Fe-C Alloys at 1150°C ," Trans., TMS-AIME (in press).
- C. H. P. Lupis and J. F. Elliott, "Oxygen-Alloying Element Interactions in Liquid Silver," Trans., TMS-AIME, 1968, Vol. 242, pp. 929-935.
- J. Chipman and J. F. Elliott, "Activity Coefficients in Dilute Strongly Bonded Metallic Solutions," Proceedings: Centennial Celebration of Tschernoff's discovery of polymorphism of iron, Moscow, May 1968.
- J. E. Sodi and J. F. Elliott, "The Free Energy of Formation of ReS_2 ," Trans., TMS-AIME, 1968, Vol. 242, pp. 2143-2145.
- F. E. Wooley and J. F. Elliott, "Mathematical Models of a Transient Thermal System," Trans., TMS-AIME (in press).
- A. Ghosh and T. B. King, "Kinetics of Oxygen Evolution at a Platinum Electrode in Lithium Silicate Melts," Trans., TMS-AIME (in press).
- M. G. Froberg, J. F. Elliott and H. G. Hadrys, "Beitrag zur Thermodynamik von Mehrstofflosungen am Beispiel homogener Eisen-Chrom-Phosphor-Kohlenstoff-Schmelzen," Archiv fur das Eisenhüttenwesen, 1968, Vol. 36, pp. 587-593.
- S. Ban-ya and J. Chipman, "Sulfur in Liquid Iron Alloys: I, Binary Fe-S," Trans., TMS-AIME, 1968, Vol. 242, pp. 940-946.
- J. Chipman, "Activity of Interstitial and Nonmetallic Solutes in Dilute Metallic Solutions: Lattice Ratio as a Concentration Variable," Trans., TMS-AIME, 1968, Vol. 239, pp. 1332-1336.
- S. Ban-ya and J. Chipman, "Sulfur in Liquid Iron Alloys: II, Effects of Alloying Elements," Trans., TMS-AIME (in press).
- S. Ban-ya and J. Chipman, "Sulfur in Liquid Iron Alloys: III, Multicomponent Systems," Trans., TMS-AIME (in press).

VII. SURFACE CHEMISTRY

Faculty:

P. L. deBruyn, Professor, Metallurgy and Materials Science

Graduate Students:

E. M. Fouquet, Graduate Student, Metallurgy and Materials Science

B. M. McLaughlin, NSF Trainee

J. W. Morris, NSF Trainee

M. Reverdy, Research Assistant, Metallurgy and Materials Science

H. Hassan, Graduate Student, Metallurgy and Materials Science

J. S. Hoch, Graduate Student, Metallurgy and Materials Science

Support Staff:

Patricia E. Gavagan, Secretary, Metallurgy and Materials Science

Personnel who have left:

E. M. Fouquet (Now in the French Army)

Degrees Granted:

E. M. Fouquet, S.M., Metallurgy, January 1968

Sponsorship:

U. S. Army Research Office-Durham, DA-31-124-ARO-D-187, DSR 75039

U. S. Army Chemical Research and Development Laboratories,

Edgewood Arsenal, DA-AMC-18-035-76(A), DSR 75276

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; E. M. Fouquet, J. S. Hoch

Sponsorship: U. S. Army Research Office-Durham

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; M. Reverdy, H. Hassan

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.

3.0 A Study of the Coagulation Behavior of Fine Powders

Personnel: P. L. deBruyn; B. M. McLaughlin

Sponsorship: U. S. Army Chemical Research and Development
Laboratories, Edgewood Arsenal

Theses:

E. M. Fouquet, "Ionic Adsorption at $Ni(OH)_2$, NiO and TiO_2 Surfaces",
S.M. Thesis, Department of Metallurgy and Materials Science,
January, 1968.

Publications:

Y. G. Berube and P. L. deBruyn, "Adsorption at the Rutile-Solution

Interface. I. Thermodynamic and Experimental Study", J. Colloid and Interface Science, 27, 305-318, June 1968.

Y. G. Berube and P. L. deBruyn, "Adsorption at the Rutile-Solution Interface. II. Model of the Electrochemical Double Layer", J. Colloid and Interface Science, 28, 92-105, September 1968.

VIII. METALS PROCESSING-CASTING AND SOLIDIFICATION

(Personnel from Department of Metallurgy and Materials Science)

Faculty:

M. C. Flemings, Associate Professor

Research Staff:

T. Z. Kattamis, Research Associate

S. N. Singh, Research Associate

W. A. Brown, DSR Research Staff

E. H. Backman, DSR Research Staff

P. R. LaFrance, Technical Instructor

Graduate Students:

D. Apelian, Teaching Assistant

L. K. Bigelow, Research Assistant

W. E. Brower, Research Assistant

A. J. Campagna, Teaching Assistant

R. Mehrabian, Teaching Assistant

S. A. Metz, Teaching Assistant

M. Myers, Teaching Assistant

M. D. Rinaldi, Teaching Assistant

A. M. Reti, Teaching Assistant

D. R. Spencer, Research Assistant

R. A. L. Troup, Teaching Assistant

J. C. Yarwood, Research Assistant

Support Staff:

R. A. Berry, Technician

A. Barbara Rich, Secretary

Personnel who have left:

P. R. LaFrance

R. A. L. Troup

Degrees Granted:

S. N. Singh, Sc.D., Metallurgy, September 1968

R. A. L. Troup, S.M., Metallurgy, August 1968

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, DA-36-038-AMC-2943(A), DSR 74963
Office of Naval Research, Nonr-3963(09), DSR 79988
U. S. Steel Grant-in-Aid, DSR 79693 (terminated 9/30/67)
American Foundrymen's Society, DSR 70438
Advanced Research Projects Agency, SD-90, DSR 78893
American Iron and Steel Institute, DSR 76379
American Iron and Steel Institute, DSR 71119 (initiated 7/1/68)

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 (Advanced Research Projects Agency)

Continuing progress has been made in establishment of the Metal Crystal Growth Facility as part of the Center for Materials Science and Engineering. One new addition to the facility is a plasma arc unit for growing metal-ceramic composite crystals.

Research on crystal growth has included continuation of study of structure of crystals grown in a magnetic field, study of growth of "composite" crystals and study of crystals grown under conditions of extremely vigorous fluid flow.

2.0 Effect of Fluid Flow in Structure (ONR)

Research is continuing on effect of fluid flow on structure of metal single crystals and of unidirectionally solidified eutectics. Convection is inhibited by application of a magnetic field and induced by crossed electric and magnetic fields. Significant improvement in perfection of the eutectic crystals is obtained by inhibiting convection.

In related work, two-phase alloys of non-eutectic composition are being grown under steep temperature gradient at slow rate and it is shown that two-phase "composites" are produced in which the second can be grown of compositions far removed from eutectic composition. Initial

work has been on lead-tin alloys; current work is on aluminum alloys of structural interest.

In addition to the foregoing, work is being conducted to study effects of extremely strong convection on solidification structures. The convection is obtained by radial solidification in the annular space between two counter-rolling cylinders ("cuvette flow"). Velocity gradient is enhanced by two orders of magnitude by superposition of a strong magnetic field.

3.0 Growth Kinetics and Structure of Metals Solidified at Large Degrees of Undercooling (Army)

Primary aim of this study is to investigate effects of large degrees of undercooling (up to 300°C) on structure and solute redistribution in metallic alloys. A secondary aim of the research is to develop improved methods for producing non-equilibrium structures (supersaturated and/or glassy structures) by rapid cooling of metallic melts.

Experimental work is currently on (a) bulk samples (approximately 100 grams) undercooled in glassy containers, and (b) levitated metal droplets. The levitated droplets are undercooled and rapidly solidified ("splat cooled") by dropping between two rapidly closing metal platens before nucleation. Current work is emphasizing nucleation and growth of non-metallic inclusions in steel solidified in the foregoing ways.

4.0 Macrosegregation (American Iron and Steel Institute)

This research comprises analytical and experimental study of macrosegregation in ingot solidification. A general expression has been obtained for segregation caused by flow of solute-rich liquid to feed solidification and thermal contractions. It is shown that inverse segregation and centerline segregation can be understood as limiting cases of the analysis, and other types of segregation also result from the fluid flow. A factor of major importance in determining segregation that has not heretofore been considered is the direction of fluid flow with respect to solidification isotherms. Experiments agree qualitatively and quantitatively with analytical results. Current work is emphasizing macrosegregation in multicomponent alloys, especially of inclusion forming elements.

5.0 Dendrite Morphology, Dendrite Arm Spacing and Grain Refinement (Army)

This program is part of a continuing study in our laboratory of dendrite structure, orientation, and grain size. Earlier work was on factors influencing final dendrite arm spacing in cast alloys and it was shown that coarsening ("ripening") exerts a major effect. Related work was on details of dendrite structures in rapidly solidified alloys. Current work is primarily on new methods of grain refinement including (a) mechanical addition of insoluble nucleating agents, and (b) electro-mechanical methods of disintegrating dendrites during growth.

6.0 Inclusions (Army, American Iron and Steel Institute)

Several related activities are under way, designed to study the formation and growth of non-metallic inclusions in metal melts (especially in steel). Inclusion 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. Also being studied is influence of inclusion morphology and chemistry on mechanical properties.

7.0 Ultra-high Strength Aluminum Alloys (Army)

Influence of solidification heterogeneities on properties of wrought aluminum alloys are being studied in this program. It has been shown that by careful control of solidification structure significant improvements in properties of wrought aluminum alloys can be obtained (e.g., tensile strengths in excess of 115,000 psi are obtained in rolled sheets. Ductility of existing alloys, especially in the transverse directions is increased several fold. A detailed electron microscopic study is in progress on fracture behavior of high strength aluminum alloys, and especially on effects of ingot heterogeneities on fracture behavior.

8.0 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.

9.0 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.

Theses:

- R. A. L. Troup, "The Dendrite-Eutectic Transition in Aluminum-Silicon Alloys," S.M. Thesis.
- S. N. Singh, "Effects of Ingot Solidification and Thermo-mechanical Processing on Properties of a Wrought High Strength Al-Alloy," Sc.D. Thesis.

Publications:

- T. F. Bower and M. C. Flemings, "Structure of Dendrites at Chill Surfaces", Trans. Met. Soc. AIME, 239, 1620-1625, 1967.
- F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt Part I," Trans. Met. Soc. AIME, 239, 1526-1533, 1967.
- F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt, Part II, Trans. Met. Soc. AIME, 239, 1534-1546, 1967.
- P. J. Ahearn, M. C. Flemings, "Dendrite Morphology of a Tin-Bismuth Alloy", Trans. Met. Soc. AIME
- T. Z. Kattamis, J. M. Coughlin, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing of Aluminum-Copper Alloys", Trans. Met. Soc. AIME, 239, 1504-1511, 1967.
- T. F. Bower, M. C. Flemings, "Double Orientation of Cast Structures", Trans. APS, 75, 1967.
- T. Z. Kattamis, M. C. Flemings, "Solidification of Highly Undercooled Castings", Trans. AFS, 75, 191-198, 1967.
- T. Z. Kattamis, U. T. Holmberg, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing and Grain Size of Magnesium-Zinc Alloy", J. Inst. Metals, 75, 343-347, 1967.
- M. C. Flemings, G. E. Nereo, "Macrosegregation Part I", Trans. Met. Soc. AIME, 239, 1449-1461, 1967.
- M. C. Flemings, R. Mehrabian, G. E. Nereo, "Macrosegregation, Part II", Trans. Met. Soc. AIME, 242, 41-49, 1968.
- M. C. Flemings, G. E. Nereo, "Macrosegregation, Part III", Trans. Met. Soc. AIME, 242, 50-55, 1968.

Accepted for Publication:

- M. C. Flemings, "Directional Solidification", Proceedings Fourteenth Sagamore Army Materials Conference, Syracuse University Press.
- M. C. Flemings, "Application of Theory to Solidification of Large Castings and Ingots", Proc. of Joint Conference on the Solidification of Metals, Brighton, England, December 4-7, 1967.

Research Reports:

- M. C. Flemings, S. N. Singh, "Effects of Solidification Variables on the Structure of Aluminum Base Ingots", Annual Report Contract No. DA-19-020-ORD-5706(A), Frankford Arsenal, Contract Period June 1967 - June 1968.
- T. Z. Kattamis, M. C. Flemings, "Solidification of Iron Base Alloys at Large Degrees of Undercooling", Contract No. DA-19-020-AMC-0231(X), Army Materials Research Agency, October 1966 - October 1967.
- M. C. Flemings, M. Myers, W. E. Brower, Jr., "Investigation of Solidification of High Strength Steel Castings", Contract No. DA-19-020-ORD-5443(X), Army Materials Research Agency, Contract Period October 1966-October 1966-October 1967.
- S. A. Metz, M. C. Flemings, "Hot Tearing", Summary Report, American Foundrymen's Society, May 1, 1967 - August 1, 1968.

IX CORROSION LABORATORY

Faculty:

H. H. Uhlig, Professor, Metallurgy and Materials Science

Research Staff:

Dr. Florian Mansfeld, Postdoctoral Fellow, Metallurgy and Materials Science

Dr. Hans Bohni, Postdoctoral Fellow, Metallurgy and Materials Science

Graduate Students:

E. W. Cook, Jr., Research Assistant, Metallurgy and Materials Science

D. J. Duquette, Research Assistant, Metallurgy and Materials Science

H. H. Lee, Research Assistant, Metallurgy and Materials Science

J. A. Marquez, Research Assistant, Metallurgy and Materials Science

T. M. Murphy, Research Assistant, Metallurgy and Materials Science

R. W. Revie, Research Assistant, Metallurgy and Materials Science

Support Staff:

Constance C. Lowery, Secretary, Metallurgy and Materials Science

Personnel who have left:

Dr. Florian Mansfeld (to NASA Research Center, Cambridge, Mass.)

Dr. Hans Bohni (to Technische Hochschule, Zurich, Switzerland)

Degrees Granted:

D. J. Duquette, Ph.D., Metallurgy, September 1968

E. W. Cook, S.M., Metallurgy, February 1968

M. Talerman, S.M., Metallurgy, February 1968

J. Antonio Marquez, S.M., Metallurgy, September 1968

Sponsorship:

Army Research Office-Durham, DA-31-124-ARO(D)-47, DSR 79341
Office of Saline Water, Grant 14-01-0001-1133, DSR 76416
Shell Companies Foundation, DSR 70816
American Iron and Steel Institute, DSR 70436
Inland Steel Fellowship, BA 21930
Sloan Fund for Basic Research in the Physical Sciences, BA 27701

Research Report

The main activities of the Corrosion Laboratory are currently concerned with:

1.0 Pitting Corrosion

Measurements and interpretation of critical potentials below which corrosion pitting of aluminum and stainless steels does not occur. Effect of environmental and metallurgical factors.

2.0 Stress Corrosion Cracking

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 the critical potentials and cracking susceptibilities of carbon and stainless steels.

3.0 Hydrogen Cracking

Effect of cold work and composition on susceptibility of alloy steels. Mechanism of failure.

4.0 Corrosion Fatigue

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 a critical corrosion rate below which the environment is not a factor.

5.0 Passivity

Effect of alloyed electron donors (non-transition elements) and of alloyed electron acceptors (transition metals) on critical composition for passivity of Cu-Ni alloys as measured potentiostatically in sulfuric acid. Relation to a reasonable interpretation of the composition and structure of the passive film.

Theses:

- D. J. Duquette, "Effect of Environment and Potential on Corrosion Fatigue of Low Carbon Steels", Ph.D., Department of Metallurgy and Materials Science, September, 1968.
- E. W. Cook, Jr., "Behavior of Various Anions as Inhibitors for Stress Corrosion Cracking of 18-8 Stainless Steels", S.M., Department of Metallurgy and Materials Science, February, 1968.
- J. A. Marquez, "Effect of Carbon Content, Heat Treatment and Cold Reduction on Hydrogen Cracking and Stress Corrosion Cracking of Ni-Fe Alloys", Department of Metallurgy and Materials Science, September, 1968.
- M. Talerman, "Stress Corrosion Cracking of Iron in Nitrates when Alloyed with C, Cu, Ge, Mo or Si", S.M., Department of Metallurgy and Materials Science, February, 1968.

Publications:

- H. H. Uhlig, "Structure and Growth of Thin Films on Metals Exposed to Oxygen", Corrosion Science 7, 325-399 (1967). Same publication translated into Russian, Zashita Metallov 5, Akademia Nauk USSR, Moscow, 516-526 (1966)
- H. H. Uhlig, "Unsolved Problems Concerning Metals Surfaces and Corrosion", J. Electrochem. Soc. 115, 108C-111C (1968).
- J. Horvath and H. H. Uhlig, "Critical Potentials for Pitting Corrosion of Ni, Cr-Ni, Cr-Fe and Related Stainless Steels", J. Electrochem. Soc. 115, 791-5 (1968).
- F. Mansfeld and H. H. Uhlig, "Passivity in Cu-Ni-Al Alloys - A Confirmation of the Electron Configuration Theory", J. Electrochem. Soc. 115, 900-904 (1968).
- D. J. Duquette and H. H. Uhlig, "Effect of Dissolved Oxygen and NaCl on Corrosion Fatigue of 0.18% Carbon Steel", Transactions ASM 51, 449-456 (1968).

X. ELECTRONIC MATERIALS LABORATORY

(All 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
J. T. A. Pollock, DSR Research Staff
A. Vejux, DSR Research Staff
F. A. Kuznetsov, Visiting Scientist (to May 10, 1968)
M. Nemeth, Visiting Scientist
T. Nemeth, Visiting Scientist
M. Santa, Visiting Scientist
J. Sochanski, Visiting Scientist (to July 19, 1968)

Graduate Students:

H. I. Andrews II, Research Assistant, Lincoln Laboratory
C. L. Balestra, Research Assistant
P. Bellin, Research Assistant
Daryl Ann Carnam, Research Assistant (to June 15, 1968)
G. T. Galyon, General Telephone & Electronics Fellow
L. Golovin, Teaching Assistant, Electrical Engineering (to August 1968)
J. McG. Harris, IBM Fellowship
D. C. Johnston, Research Assistant (to September 1967)
L. C. Kimerling, Research Assistant
L. Kiss, Graduate Student
I. Lagnado, Graduate Student
D. Miller, Research Assistant
N. Platakis, Research Assistant
E. R. Pollard, Research Assistant, Lincoln Laboratory (to January 1968)
O. Sandven, Graduate Student
R. Singh, Research Assistant
S. Spitzer, Graduate Student, Electrical Engineering
J. J. Stickler, Research Assistant, Lincoln Laboratory (to July 1968)

T. M. Valahas, Research Assistant

Support Staff:

J. Baker, Technician
 W. J. Fitzgerald, Engineering Assistant
 C. J. Herman, Engineering Assistant
 T. W. Stewart, Technician
 Susan E. Haroian, Secretary
 Rachel A. Saxe, Secretary (to February 9, 1968)

Degrees Granted:

Daryl Ann Carnam, S.M., Metallurgy, June 1968
 L. Golovin, S.M. and EE, Electrical Engineering, September 1968
 E. R. Pollard, Ph.D., Metallurgy, January 1968
 R. Shull, S.B., Metallurgy, June 1968
 J. J. Stickler, Sc.D., Metallurgy, June 1968
 D. C. Johnston, S.M., Metallurgy, September 1967

Personnel who have left:

Daryl Ann Carnam, Research Assistant (Now a Special Student,
 Metallurgy at MIT)
 L. Golovin, Teaching Assistant (Now a Graduate Student, Sloan School
 of Management at MIT)
 E. R. Pollard, Research Assistant (Now at Ion Physics, Burlington,
 Massachusetts)
 J. J. Stickler, Research Assistant (Now at Naval Architecture Depart-
 ment, MIT)
 D. C. Johnston, Research Assistant (Now Administrative Officer,
 Department of Metallurgy)

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75122, 75126, 78896
 Lincoln Laboratory AF 19(628)-5167(part) (expires September 15, 1968)
 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 79450
 National Science Foundation GK-1653, DSR 70399
 Wright-Patterson Air Force Base F33 615-69-C-1031, DSR 71300

Research Report1.0 Elemental and Compound Semiconductor Surfaces

Personnel: Professors H. C. Gatos, A. F. Witt; Dr. J. Sochanski; C. L. Balestra, T. M. Valahas, S. Spitzer

Sponsorship: Office of Naval Research and Advanced Research Projects Agency

Our research on the characterization of elemental and compound semiconductor surfaces was centered on Ge, GaAs and CdS.

In order to facilitate the interpretation of field effect signals the feasibility of analog processing was investigated. By using a logarithmic transducer we could thus convert the exponential decay of surface conductivity into a line of constant slope. In the course of this investigation we developed a high resistance-low capacitance input amplifier which permitted the recording of surface photovoltages on existing oscillographic equipment.

Large signal alternating current field effect experiments in the dark and under illumination were carried out on "real" germanium surfaces following a heat treatment in ultrahigh vacuum. After prolonged heating (about 10 hours) at 520°K, the surfaces were slightly p-type, exhibiting 3 to 5 times higher density of traps than prior to heating. Higher temperatures (560°K, 600°K and 640°K) rendered the surfaces more p-type, but caused essentially no change in the density of traps. The observed changes of the electrical properties were correlated to the results of desorption experiments in which a mass spectrograph was employed. The total surface charge was found to increase linearly with the amount of desorbed water.

Real gallium arsenide surfaces were investigated by means of the field effect experiment in the temperature range from -50°C to +200°C. High voltage alternating current field effect experiments were performed. They did not reveal the conductance minimum which indicates the exact equilibrium value of the surface barrier cannot be determined under the present conditions. It was found that in darkness, the kinetics of surface states bulk interaction (for n-type GaAs) is governed by the majority carriers and that the thermal excitation process dominates. Under illumination, the minority carriers (holes) become effective and the interaction of the holes with the surface states plays the dominant role.

A discrete "fast" state was found in the middle of the energy gap (.70 eV from the conduction band) with an equilibrium number of carriers of about 10^{11} cm^{-2} and a very large capture cross section, 10^{-12} cm^2 corresponding

to an attractive center. The presently observed surface states appear to be of crystal defect origin rather than of the abrupt termination of the lattice periodicity.

In connection with the surface characterization of CdS, an intensive study of its etching characteristics was undertaken. It was found that relatively smooth "S" surfaces can be obtained with an etching solution of 0.5 M $K_2Cr_2O_7$ and 12N H_2SO_4 at 95°C. This etching procedure, however, results in pronounced conical etch pits on the "Cd" surface. Greatly improved flatness could be obtained by using concentrated H_3PO_4 at temperatures in excess of 160°C. This process yielded exceptionally smooth surfaces. The disadvantage of the orthophosphoric etching process is its lack of adequate reproducibility and its great sensitivity towards surface orientation. Deviations of less than 1° from the basal plane orientation result in "rough" surfaces (etch-pits) even after short etching times. The reproducibility problem is still under investigation.

CdS doped with In (Eagle-Pitcher Company) was electrically characterized in temperature range between 77° and 373°K. Low temperature Hall data indicate a donor level of .04 eV below the conduction band edge. The donor concentration was $3.6 \times 10^{17} \text{ cm}^{-3}$. The electron mobility could be represented as $7.42 \times 10^5 \times T^{-1.37}$, $\text{cm}^2/\text{volt-sec}$, above 140°K. The room temperature conductivity was found to be $3.5\Omega^{-1} \text{ cm}^{-1}$.

2.0 Crystallochemical Approach to Electronic Materials

Personnel: Professors H. C. Gatos, A. F. Witt; Dr. J. T. A. Pollock; P. Bellin, D. Carnam. N. Platakis, G. Galyon

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

2.1 Superconductors

An investigation to determine the effect of second phase precipitation on the superconducting critical temperature (T_c) and critical current density (J_c) of well annealed binary transition metal alloys has been undertaken. Two systems have been chosen: Ta rich-Zr alloys, where the Zr rich phase which precipitates on ageing supersaturated solid solutions is normal at 4.2°K; Zr rich-V alloys, where the matrix phase is normal at 4.2°K and the stable precipitate is a Cl5 intermetallic compound of stoichiometry V_2Zr and is superconducting below 8.5°K. Optical and electron microscopy and x-ray diffraction techniques are being used to investigate the nature and distribution of the precipitating phase.

Metallography indicates that precipitation in the Ta-Zr system is of the continuous type. This is confirmed by the T_c measurements on the same specimens. J_c data for this system shows that depending on the initial degree of supersaturation ageing at 350° and 500°C results in enhancement of the critical current density by almost an order of magnitude. The peak in J_c is found to coincide with a precipitate particle size and separation of 1 micron.

Precipitation in the Zr-V system is complicated by a martensitic transformation which occurs when the alloys are quenched from the solution temperature (1100°C). The T_c and J_c data indicate that the behavior of the alloys on ageing at 500°C depends strongly on the degree of supersaturation. Alloys containing <6 a/o V exhibit variations in T_c and J_c on ageing which appear to be characteristic of a complex precipitation process. The metallographic investigation of this system will continue in an effort to correlate the variations in T_c and J_c with the ageing process.

Following the determination of the transition temperature, T_c , and the upper critical field, H_{c2} , as a function of composition in the ternary system Ti-Nb-V, a study of a representative sample 40% Ti- 30% Nb- 30%V was conducted. The critical current, J_c , in a transverse field as a function of rotation around the strip sample axis has been measured with the strip axis both in and perpendicular to the rolling direction. Heat treatment for 24 hours resulted in a.) no change in T_c and H_{c2} at 450°C, b.) a drop in H_{c2} from 84 k gauss to 66 k gauss at 1000°C, c.) a further drop to 41 k gauss at 1600°C. Due to recrystallization the critical current was no longer a function of orientation for the samples annealed at 1000°C and 1600°C. The grain boundaries are the dominant flux pinners. A secondary peak in J_c (α) was found with the current parallel to the rolling direction but not when the current was perpendicular to it. Previous explanations fail to account for this result.

Annealing at 1600°C for several different compositions resulted in decreases in T_c of the order of one degree. Resistivity measurements on the cold-rolled material determined that the binary alloys had lower values of normal state resistivity, ρ_n , than the ternary alloys, and that ρ_n increased with Ti concentration.

The variation of T_c was found to be consistent with the concept of a collective d band. The variation of the shape of the functions $T_c(n)$ and $H_{c2}(n)$, where n is the number of electrons/atom outside of filled bands, were used in conjunction with lattice parameter and resistivity data to predict changes in the shape of the d band. The transition temperatures

have been used to determine the variation with composition of $N(0)V$, the density of states at the Fermi surface multiplied by the electron-phonon-electron interaction parameter of the Bardeen-Cooper-Schrieffer theory. It was found that the effective valence concept of DeSorbo is not applicable to this system.

H_{c2} and T_c were related by an equation $H_{c2}/T_c = f_i(n)$. Three distinct functions $f_i(n)$ were found for the Ti-Nb-V system -- one for each of the binaries, Ti-Nb and Ti-V, and one for the ternary alloys. This result has been related to the theoretical work of Gorkov.

2.2 Semiconductors

The work on vitreous semiconductors is being continued with the system $xAs_2Se_3.ySb_2Se_3$. The optical activation energies have been found from the fundamental light absorption edges as a function of composition and temperature using the indirect transition theory which is applicable to these systems. The agreement between the optical activation energies and the thermal activation energies, which we found previously from resistivity versus temperature measurements, is excellent. The thermal coefficient of the optical activation energies is $7.5 \times 10^{-4} \frac{eV}{^\circ C}$. The activation energy decreases with increasing Sb_2Se_3 content. It is higher in the vitreous state than for the crystalline state by 0.2 to 0.4 eV.

Infrared transmission, absorption and reflection have been investigated as a function of composition and temperature in the regions 0.6-1.6 μ and 2.5-50 μ . No absorption or reflection bands were observed. The fundamental absorption edges occur in the region 0.6-1 μ , their exact position depending on the composition and temperature.

3.0 Distribution of Impurities in Solids

Personnel: Professors H. C. Gatos, A. F. Witt; L. Kimerling, R. Singh, D. Miller, J. Sandor

Sponsorship: Advanced Research Projects Agency, National Science Foundation, Air Force Systems - ASD

Our investigation of the single crystal growth characteristics in Czochralski-type crystal pulling systems is being continued. Polishing (mechanical and chemical) techniques together with differential etching were combined with interference contrast microscopy and multiple beam interferometry in the study of the microdistribution of impurities in semiconductor single crystals. A linear resolution of better than 2000 Å is now reproducibly achieved. Under this resolution impurity heterogeneities

heretofore unknown were discovered. Their origin was theoretically related to the growth conditions. A technique was developed which, for the first time, allowed the determination of the microscopic (instantaneous) growth rates. In this way it was possible to relate experimentally the incorporation and distribution of dopants, on a microscale, to the localized growth conditions. The dopant microheterogeneities discovered are believed to account for some anomalies in the electrical behavior of certain semiconductors. A study of the modes of crucible and seed rotation led to conditions resulting in single crystals in which no impurity heterogeneities could be observed by all available techniques.

Our research on impurity distribution in semiconductors has been expanded to germanium. An etching technique was developed to resolve impurity heterogeneities in Ga doped Ge single crystals. The specific etchant is $10 \text{ H}_2\text{O}_2$ (30%) + 10 HF (48%) + $25 \text{ H}_2\text{O}$. Two minutes etching time at room temperature was found suitable. Studies of the instability of the growth interface due to constitutional supercooling are currently carried out. It was found that instability of the interface increases with increasing pulling rate and decreasing rate of seed rotation.

Also under investigation is the effect of applied electric fields across the growth boundary in InSb. Of particular interest is their effect on impurity distribution coefficients.

The electrical properties of InSb with varying degrees of impurity inhomogeneity are currently studied. Preliminary Hall measurements show that crystal sections grown under seed rotation (striated) exhibit considerably lower charge carrier mobilities than sections grown with crucible rotation (non-striated). In crystals grown with seed rotation alone it was observed that the carrier mobility in "on core" regions is higher than that in off core regions.

Our investigation of radiation induced compensation in "high purity" Ge single crystals is being continued. High purity single crystals of germanium have been grown in this laboratory for the study with net carrier concentrations as low as $5 \times 10^{11} \text{ cm}^{-3}$ (p-type) and $4 \times 10^{12} \text{ cm}^{-3}$ (n-type). We have prepared radiation detectors which have a resolution of <2% for the Cs^{137} spectrum and show no decrease in resolution upon storage for several hours at room temperature.

A study of the introduction of radiation defects into germanium has revealed that the introduction rate is strongly dependent on initial carrier concentration.

4.0 Semiconductor Growth and Characterization

Personnel: Professors H. C. Gatos, A. F. Witt; M. Lichtensteiger, J. M. Harris, G. Galyon

Sponsorship: Advanced Research Projects Agency

Research on epitaxial vapor growth of silicon carbide is being continued. The present phase of the study is concerned with the etching characteristics of SiC. It was found that the etch rate of single crystal α -SiC in H_2 follows an Arrhenius type dependence on temperature and is also a function of the susceptor employed, with graphite giving the lowest and molybdenum the highest etch rates. W, Ta, and Nb exhibit intermediate rates of etching.

Single crystalline α -SiC layers have been grown on α -SiC substrates at 1500°C. At higher temperatures the simultaneous etching rate of the substrate becomes too high for any net deposition to take place. It is believed that this critical temperature is a function of gas dynamics and reaction kinetics. This aspect is currently under investigation.

Work on single crystal growth of pseudobinary III-V compound semiconductors (Ga-In-Sb) is continued. Our experiments showed that the most critical parameter for successful crystal growth is the rate of pulling. At growth rates of less than 0.55 cm now it was possible to obtain single crystals with up to 10% InSb in the GaSb lattice. At higher rates constitutional supercooling induces polycrystallineity. At present the onset of interface instability associated with constitutional supercooling is being investigated by means of the rate striation technique.

The surface damage induced during polishing of the "A" and "B" surfaces of InSb single crystals is being investigated by anomalous x-ray transmission. The induced dislocation density in the damaged layers was found to be too high to be resolved by the conventional photographic techniques. The integrated intensities are therefore recorded by a counter and are related to an "average" burgers vector of the dislocations. It was shown experimentally that the peak half widths are not effected by the abrasion process. Thus, the integrated intensities obtained by count recording can be directly related to the time averaged peak intensities obtained by the photographic method. The sensitivity of the method is currently being assessed.

Theses

- D. Carnam, "A Study of the Relationships between Superconductivity and Electronic Structure in the Nonmagnetic Transition Metal Carbides", S.M. Thesis, Department of Metallurgy and Materials Science, June 1968.
- L. Golovin, "A Germanium Radiation Detector Produced by Gamma-Ray Irradiation Damage", S.M. Thesis, Department of Electrical Engineering, August 1968.
- E. R. Pollard, "Electronic Properties of Niobium Monoxide", Ph.D. Thesis, Department of Metallurgy and Materials Science, January 1968.
- R. Shull, "The Effects of Precipitation on the Superconducting Parameters of the Vanadium-Zirconium Binary System", B.S. Thesis, Department of Metallurgy and Materials Science, June 1968.
- J. J. Stickler, "Spin Resonance in Spiral-Spin Structure Compounds", Sc.D. Thesis, Department of Metallurgy and Materials Science, June 1968.

Publications

- A. F. Witt and H. C. Gatos, "Microscopic Rates of Growth in Single Crystals Pulled from the Melt: Indium Antimonide", J. Electrochem. Soc. 115, 70 (1968).
- R. Singh, A. F. Witt and H. C. Gatos, "Application of the Peltier Effect for the Determination of Crystal Growth Rates", J. Electrochem. Soc. 115, 112 (1968).
- V. Sadagopan and H. C. Gatos, "New Infra-Red Transmitting Phosphovanadate Glasses Containing Rare Earth Oxides", Mat. Sci. and Eng. 2, 273 (1968).
- D. C. Johnston, A. F. Witt and H. C. Gatos, "Impurity Heterogeneities and Multiple-Beam Interferometry", J. Electrochem. Soc. 115, 438 (1968).
- R. S. Mroczkowski, A. F. Witt and H. C. Gatos, "Effects of Back-Melting on the Dislocation Density in Single Crystals: GaSb", J. Electrochem. Soc. 115, 545 (1968).
- K. Morizane, A. F. Witt and H. C. Gatos, "Impurity Distribution in Single Crystals IV. Growth Characteristics and Impurity Incorporation During Facet Growth", J. Electrochem. Soc. 115, 747 (1968).
- H. R. Huff, S. Kawaji and H. C. Gatos, "Electronic Configuration of Indium Antimonide Surfaces", Surface Science 10, 232 (1968).

- R. S. Mroczkowski, A. F. Witt and H. C. Gatos, "Accommodation of Lattice Mismatch at Heterojunctions", J. Electrochem. Soc. 115, 750 (1968)
- H. C. Gatos, "The Scientific Society through the Centuries", J. Electrochem. Soc. 115, 180C (1968).
- H. R. Huff, S. Kawaji and H. C. Gatos, "Relaxation Phenomena on Indium Antimonide Surfaces at High Electric Fields", Surface Science 5 (1968).
- F. T. J. Smith and H. C. Gatos, "Surface Superconductivity in Tantalum", J. Appl. Phys. 39 (1968).
- A. F. Witt and H. C. Gatos, "Germanium", "The Encyclopedia of the Chemical Elements" ed. by C. A. Hampel, Reinhold Book Corporation, New York, pages 237-244 (1968).
- A. F. Witt and H. C. Gatos, "Microdistribution of Dopants in Semiconductor Single Crystals: InSb", International Semiconductor Conference, Moscow, 1968, in press.
- V. Sadagopan and H. C. Gatos, "Average Heat of Atomization and the Properties of Semiconductors", "Chemical Bond in Crystals" 1968, in press.
- H. R. Huff, S. Kawaji and H. C. Gatos, "Observation of Quantum Galvanomagnetic Phenomena in N-Type Indium Antimonide", Physica Status Solidi, in press.
- J. Sochanski and H. C. Gatos, "Effect of Thermal Desorption of Water Surface States on Germanium in Ultra-High Vacuum", Surface Science, in press.
- L. Kimerling, L. Golovin and H. C. Gatos, "Germanium Radiation Detectors Compensated by Irradiation Defects", Proceedings of the IEEE, in press.
- J. T. A. Pollock, H. W. King, F. H. Cocks, "Further Evidence of the Low Temperature Phase Transformation in Nb_3Sn and V_3Si ", Phys. Letters 26A, 77 (1967).
- J. T. A. Pollock, H. W. King, "Low Temperature Martensitic Transformations in In/Tl Alloys", J. Mat. Science 3 372 (1968).

XI. SUPERCONDUCTIVE MATERIALS

(Personnel from Department of Metallurgy and Materials Science except where indicated)

Faculty:

J. Wulff, Professor
R. M. Rose, Associate Professor
L. W. Gruenberg, Associate Professor, Electrical Engineering

Research Staff:

T. H. Courtney, Research Associate
L. A. Shepard, DSR Staff

Graduate Students:

S. Foote Snow, Research Assistant
G. Goetz, Research Assistant
J. Hafstrom, Teaching Assistant
K. A. Jones, Research Assistant
D. D. Morrison, Allegheny Ludlum Fellow
S. Ochiai, Research Assistant
J. Pearson, Research Assistant
G. C. Rauch, U. S. Steel Fellow
R. Ricketts, Teaching Assistant
H. Shih, Research Assistant
W. R. Stowell, Teaching Assistant
L. Weinman, Teaching Assistant

Support Staff:

S. Jackson, Student Assistant, Physics
B. R. Rose, Student Assistant
I. M. Puffer, Engineering Assistant
Phyllis M. Stratton, Secretary

Personnel who have left:

T. H. Courtney (to Dept. of Mechanical Engineering, University of Texas
Austin, Texas)
S. Foote Snow

K. A. Jones (to 3M Central Research Laboratories, St. Paul, Minn.)
G. C. Rauch (to Research Center, U. S. Steel Corp., Monroeville, Pa.)
Shirley Jackson (to Physics Department, MIT)
B. R. Rose (to Aeronautical and Astronautical Engineering Dept., MIT)

Degrees Granted:

K. A. Jones, Ph. D., Metallurgy, June 1968
G. C. Rauch, Sc. D., Metallurgy, February 1968
S. Foote Snow, S. M., Metallurgy, September 1968
S. Jackson, S. B., Physics, June 1968
B. R. Rose, S. B., June 1968

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75124
National Science Foundation, GK 1073, DSR 76350, terminated: GK 1071,
DSR 76353, terminated; GK 1688X, DSR 70568; GK2911, DSR 71029
Office of Naval Research, Nonr 3963-16, DSR 74611

Research Report:

1.0 High-Field Solid Solution Superconductivity

1.1 Aging in Nb-Ti-O Superconductors

The superconducting behavior of Nb-Ti alloys containing 40 and higher wt. pct. of Nb and variable oxygen content was studied as a function of thermomechanical processing. Critical current density (J_c) vs. applied transverse magnetic field (H) data were obtained for 0.010 in. diameter wires at 4.2 degrees K in steady fields up to 120 kiloersteds. The precipitate responsible for increase in J_c in each of the alloys studied was related to niobium and oxygen content.

In alloys containing 40-60 wt. pct. Nb with less than about 1600 ppm. of oxygen, omega precipitation in the range 350-405°C appears to be responsible for the maximum value of J_c observed. In alloys of higher oxygen content (~2500 ppm.), the oxygen enriched alpha phase which precipitates in the temperature range 450-550°C is a more effective fluxoid pinner. Maximum J_c in low oxygen(350 ppm.) 80 wt. pct. Nb alloys was achieved by 600°C aging heat treatments. Measurements of resistive critical field also reflect the changes in composition accompanying precipitation in these alloys.

1.2 Yttrium, Lanthanide and Actinide Additions to Nb-Ti-O Alloys

The addition of metals such as Y, Gd or Th to Nb-Ti-O alloys raises the general level of J_c markedly, and simultaneously may improve the ductility. This is particularly significant in view of new processing requirements for the manufacture of composite magnet wires of Cu and superconducting alloys. The model we propose to explain such behavior is the appearance of an oxide precipitate of the quaternary metal addition, and the reduction of oxygen in solution in the Nb-Ti- matrix. We are presently testing this model, and, we hope, developing solid solution superconductors of still higher J_c and ductility.

2.0 Superconductivity in the Transition Metals

Sponsorship: National Science Foundation

2.1 The Critical Field of Nb

Severely cold-worked Nb may remain superconducting up to applied fields of $4H_{c2}$ and more. This cannot be explained by applying the GLAG theory to the changes in bulk properties, nor by postulation of "internal surface" nucleation, which could at best persist to $1.7 H_{c2}$. We are presently investigating this phenomenon and its relation to microstructure, and are fabricating Nb in which the plastic deformation is greater than has heretofore been obtained, as a "limiting case".

2.2 Oxygen in Nb

We have succeeded in controlling oxygen contamination by growing and heat-treating single crystals in ultra-high vacua. Our measurements, ultrasonic, resistive and J_c , confirm the hypothesis that oxygen atoms cluster in Nb, even at concentrations below 500 ppm. The pinning or Lorentz force parameter (α) is largest when $J \times B$ is normal to the habit plane or boundary of the clusters.

2.3 The "Peak Effect"

The J_c peak in the above crystals occurred only when the clusters had grown to a size considerably in excess of that necessary for optimal

fluxon-pinning; presumably, about an order of magnitude more than the coherency distance. To confirm that this feature is essential to the appearance of the peak, we are now conducting controlled experiments on Pb-Ti alloys.

2.4 Superheating of the Meissner State

We have measured the delay of the Meissner-Mixed state transition in V, Nb and Ta crystals and found that in all cases the superheating field is more than H_c , in direct contradiction of much of the theory, and partially confirming the work of the Orsay Group.

3.0 Tunneling

Sponsorship: Office of Naval Research

3.1 Nb Single Crystals

We have now mapped the gap parameter over the complete stereographic triangle. The principal features in the $\Delta(k)$ contour coincide with those of the recently proposed group V Fermi surface. In addition, non-BCS gap behavior is observed, and low-energy detail appears which suggests multigap-multiband behavior. To explore these possibilities, we are performing measurements at .5°K and below, on purer crystals.

3.2 V Single Crystals

Although V crystals of resistivity ratios of 100 and better can now be grown, we have not succeeded in growing good tunnel junctions.

3.3 Alloys

Limited success has been attained with thermally grown oxides as tunneling barriers on Nb-Ti alloys. We are presently attempting to use CdS, Al_2O_3 or other 'artificial' barriers to improve the yield of "good" junctions.

4.0 Superconducting Composites

Sponsorship: Advanced Research Projects Agency

The magnetic behavior, critical fields and critical temperatures of our Nb-Cu composite have now been measured in detail, and completely fit a model based on the proximity effect theory of the Orsay group, and the known geometry of the composite. Laminar composites are also being investigated.

5.0 High T_c and Structure

Sponsorship: Advanced Research Projects Agency

Many thin films (e. g. , Al) have critical temperatures very much larger than the corresponding bulk material. Some metals do not exhibit this phenomenon. Although it is reasonable to attribute the high T_c behavior to abnormal structure, no direct evidence of the nature of the structure is now available. We are presently performing X-ray and electron diffraction, and electron micrography on high- T_c and low- T_c Al films made in our laboratory. Other techniques, e. g. interference contrast micrography will also be used, if necessary. We intend to delineate the structural mechanism (if one exists) for high T_c in thin films and hopefully bulk superconductors as well.

Publications:

- B. P. Strauss and R. M. Rose, "Proximity Effects in a Fine Composite", Phys. Letters, 25A, 362 (1967).
- B. P. Strauss and R. M. Rose, "Strong Proximity Effects in Cu: Superconductivity of a Fine Nb-Cu Composite", J. App. Phys. 39, 1638 (1968).
- M. L. A. MacVicar and R. M. Rose, "Measurement of the Anisotropic Energy Gap in Nb Single Crystals", Proc. Symposium on Physics of Superconducting Devices, B. S. Deaver, Jr. and W. S. Goree, eds., ONR, 1967, p. Q-1.
- M. L. A. Mac Vicar and R. M. Rose, "Anisotropy of the Nb Energy Gap by a Single Crystal Tunneling Technique", Phys. Letters 25A, 681 (1967).

- M. L. A. MacVicar and R. M. Rose, "Anisotropic Energy Gap Measurements on Superconducting Nb Single Crystals by Tunneling", *J. App. Physics* 39, 1721 (1968).
- M. L. A. MacVicar and R. M. Rose, "Detail in the Tunneling Characteristics of Superconducting Nb Single Crystals", *Physics Letters* 26A, 510 (1968).
- K. A. Jones and R. M. Rose, "The Paek Effect and the Clustering of Dissolved Oxygen in Superconducting Nb", *Physics Letters* 27A, 414 (1968).
- T. H. Courtney and J. Wulff, "Quarternary Solid Solution Superconductors", *Physics Letters* 25A, 477 (1968).

Accepted for Publication

- K. A. Jones, S. C. Moss and R. M. Rose, "The Effect of Small Oxygen Additions on the Elastic Constants and Low Temperature Ultrasonic Attenuation of Nb Single Crystals", to appear in *Acta Met.*
- K. A. Jones and R. M. Rose, "The Anisotropy of the Critical Current Density of Superconducting Oxygen-Doped Nb", to appear in *Trans. Met. Soc. AIME*.
- B. P. Strauss and R. M. Rose, "Proximity Effects in Multiphase Materials", to appear in Proc. XIth Int. Conf. on Low-Temp. Physics.
- M. L. A. MacVicar and R. M. Rose, "Tunneling into Nb Single Crystals", to appear in Proc. XIth Int. Conf. on Low-Temp. Physics.
- G. C. Rauch, T. H. Courtney, and J. Wulff, "Aging in Nb-Ti-O Superconductors", and Appendix: G. C. Rauch, R. L. Ricketts, T. H. Courtney, and J. Wulff, "Rate of Aging in Nb-Ti-O Superconductors", to appear in *Trans. Met. Soc. AIME*.
- L. C. Skinner II and R. M. Rose, "Improvements in the Floating-Zone Electron Beam Technique for the Group V Refractory Metals", to appear in Proc. 2nd Int. Conf. on Electron and Ion Beam Science and Technology.

XII. CERAMICS

(All personnel from Department of Metallurgy and Materials Science.)

Faculty:

R. L. Coble, Associate Professor
W. D. Kingery, Professor
C. J. Mogab, Assistant Professor
D. R. Uhlmann, Assistant Professor
B. J. Wuensch, Assistant Professor

Research Staff:

T. P. Jones, Visiting Scientist
T. J. Brown, Engineering Assistant

Graduate Students:

H. T. Anderson, Research 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
T. R. Guillermo, Instructor
R. M. Hakim, Research Assistant
R. N. Katz, Graduate Student
G. A. Kemp, Research Assistant
K. S. Kim, Research Assistant
I. Kohatsu, Research Assistant
W. T. Laughlin, Research Assistant
J. H. Li, Research Assistant
J. K. Michel, Research Assistant
A. M. Mocellin, Research Assistant
R. L. Poher, Research Assistant
S. Prochazka, Research Assistant
J. J. Rasmussen, Research Assistant
W. L. Robbins, Research Assistant

J. Sauvage, Research Assistant
 R. J. Tiernan, Research Assistant
 P. J. Vergano, 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. L. Anderson (Now at IBM, White Plains, New York)
 R. M. Hakim (Now to Hydro-Quebec, Montreal, Canada)
 T. P. Jones (Now at Commonwealth Scientific and Industrial Research
 Organization, Chippendale, Australia)
 S. Prochazka (Now at Tibor, Czechoslovakia)
 M. Safdar (Now at West Regional Labs., Lahore, Pakistan)
 R. R. Shaw (Now at American Optical Company, Southbridge, Mass.)

Degrees Granted:

R. M. Hakim, Ph.D., Ceramics, September 1968
 D. S. Gelles, S.M., Ceramics, January 1968
 S. Prochazka, S.M., Ceramics, June 1968

Sponsorship:

The research is sponsored by the following agencies. Specific sponsorship is also listed under each individual research report.

Atomic Energy Commission, Contract No. AT(30-1)-3773, DSR 70112
 National Science Foundation, Contract No. GA1549, DSR 71042
 National Defense Education Act Fellowship

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

Personnel: R. L. Coble, W. D. Kingery, C. J. Mogab, D. R. Uhlmann, and B. J. Wuensch; T. J. Brown, K. S. Kim, J. K. Michel, R. L. Poher, S. Prochazka, W. L. Robbins, R. J. Tiernan, P. J. Vergano, and J. Sauvage

1.1 Grain Boundary Diffusion Studies

Personnel: B. J. Wuensch; R. J. Tiernan

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Polycrystalline bodies are usually involved in the practical situations in which diffusion may be a rate-controlling process. In such materials preferential diffusion along grain boundaries may greatly modify rates predicted on the basis of single-crystal diffusion data. Direct evidence for grain boundary diffusion has been obtained for only a few ionic materials and oxides. The role of grain boundary chemistry and grain orientation in the effect is not clear.

Diffusion rates for Tl (a highly polarizable ion for which transport should be greatly influenced by the presence of grain boundaries) have been studied in single-crystal, bicrystal and polycrystalline KCl. The Tl solute was supplied either from an initial thin film of TlCl or through equilibration of a surface of the specimen with a vapor of TlCl.

Temperature ranges of both intrinsic and extrinsic behavior were found for Tl diffusion in single crystal KCl. The diffusion coefficient in these regions could be described by

$$D = 6 \cdot 10^{-3} \exp (-1.42 \text{ eV/kT})$$

$$D = 9 \cdot 10^{-11} \exp (-0.25 \text{ eV/kT})$$

respectively. These results provide 2.34 eV as the energy required for Schottky defect formation, a value in good agreement with estimates of other

workers. Enhanced diffusion along grain boundaries was observed in some, but not all samples. Typical values of the product of grain boundary width and grain boundary diffusion coefficient were small: of the order of 1 to $20 \times 10^{-14} \text{ cm}^3/\text{sec}$ at temperatures in the range 550 - 685°C , and were not a function of solute concentration. The degree of enhancement was erratic and not reproducible, and probably arose from impurities at the grain boundary. Bicrystals intentionally synthesized in the presence of water vapor show marked enhancement of the degree of boundary diffusion.

1.2 Transport in Crystals Subjected to Stress

Personnel: B. J. Wuensch; K. S. Kim

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The stress imposed on ceramics during processing or in their applications could conceivably alter transport rates in a number of ways. Experiments performed with metals indicate that, at low temperatures, diffusion rates are independent of strain, but may be enhanced by several orders of magnitude by high strain rates. Diffusion data for strained ionic materials are not available. It is known, however, that the conductivity may be modified by deformation (the Gyulai-Hartly effect). The mechanism of the enhancement is complex and still open to question. Interpretations which have been advanced include flow of charged dislocations, polarization of dislocation charge, and dissociation of impurity-vacancy complexes.

In the present program an attempt will be made to study the defect structure of deformed alkali halides through simultaneous measurement of both self-diffusion rates and electrical conductivity. Equipment has been assembled to permit measurements of conductivity of crystals during either compression or tension.

1.3 Effect of Pressure on Grain Boundary Self-Diffusion

Personnel: R. Coble; R. L. Pober

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773, DSR 70112

The purpose of this investigation is to determine the effect of hydrostatic pressure on grain boundary self-diffusion. Since grain boundary

diffusion is undoubtedly an important mechanism in densification during hot-pressing, it is necessary to understand the effect of pressure on this mechanism in order to have a better understanding of the process of hot-pressing. It is also hoped to gain some information about the atomic processes of grain boundary diffusion and the structure of grain boundaries.

A study of the various techniques used to determine grain boundary diffusivity indicates that the best one for studying self-diffusion is radio-isotope diffusion, followed by sectioning and counting. Initial experiments to determine the grain boundary diffusivity as a function of pressure and temperature will be performed in an internally heated "bomb" which is being designed.

Determination of the grain boundary diffusivity by various means requires the knowledge of the lattice diffusivity and the effect of pressure. For this reason the materials chosen for the study are silver and lead.

Experiments will be performed with single crystal and polycrystal specimens simultaneously. If possible, bicrystals will also be used in each experiment.

1.4 Sintering Kinetics of Alumina by Surface Measurement

Personnel: R. Coble; S. Prochazka

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

An increase of gas permeability in fine grained alumina compacts was observed when heated below the temperature of the initial shrinkage. The effect depends strongly upon density. The measurements are presented as surface area decrease and related to surface diffusion in alumina by means of two models, assuming sintering of spheres and cubes respectively.

The surface self-diffusion coefficient calculated from the sintering spheres model is:

$$D_S = 4.8 \times 10^{-2} \exp \left[\frac{(5.6 + 0.6) \times 10^4}{RT} \right] \text{cm}^2/\text{sec}$$

The other model yields values larger by a factor of three.

At higher temperatures a permeability maximum was found after the compacts underwent about 3% shrinkage. The percent permeability maximum was linked to the termination of pore shape development.

1.5 Grain Boundary Diffusion in Polycrystalline Alumina

Personnel: R. Coble; W. L. Robbins

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

Grain boundary diffusion plays an important role in many ceramic processes, but as yet there is little or no quantitative information for values of the grain boundary diffusion coefficients in ceramic systems other than those for self-diffusion. The need for this information is obvious in order to thoroughly understand such processes as sintering, grain growth, recrystallization, homogenization, dissolution, creep, and electrical conductivity in ceramics.

With this in mind, it has been proposed that the coefficient for grain boundary diffusion in polycrystalline alumina can be determined. The work by T. P. Jones has demonstrated that a defect diffusion coefficient can be determined in single crystal alumina by the observation of a color boundary migration due to the oxidizing or reducing conditions at the surface of a crystal. In doped polycrystalline alumina samples a similar migration of a color boundary has been observed. The rate of movement is greater than that for the single crystals which indicates that there is enhanced diffusion in the grain boundaries, a phenomena which has been observed in many other systems.

In addition to polycrystalline specimens, single crystals have been grown and further diffusion studies in both areas will be expedited by the use of a thermal gradient furnace built during the past year. These diffusional studies will be correlated with electrical conductivity information in an effort to obtain a thorough understanding of transport in polycrystalline alumina.

1.6 Kinetics of Processes Characterized by a Distribution of Activation Energies

Personnel: W. D. Kingery, C. J. Mogab; J. Sauvage

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

Good examples of processes characterized by a distribution of

activation energies may be found in evaporated thin films. The conductivity of amorphous thin films of silicon or germanium is to be recorded during four or five decades of time in logarithm scale at annealing temperatures of 20°C up to 500°C. A thin film heater characterized by a short time constant and a good stability around the operating temperature will be included in the evaporation system. Steady-state annealing temperature is therefore quickly obtained and closely maintained. An effort will be made to fit the data to distributions of activation energies, followed by interpretation in terms of quantum mechanical models of conduction.

1.7 Densification of Nonstoichiometric Magnesia-Aluminate Spinel Powder Compacts

Personnel: W. D. Kingery and J. K. Michel

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

The stability field of $\text{MgO-Al}_2\text{O}_3$ spinel extends over a wide range from MgO -rich to Al_2O_3 -rich spinel. Drastically different sinterability of powder compacts consisting of variable ratios of $\text{Al}_2\text{O}_3/\text{MgO}$ has been observed.

It has been found that, to densify powder compacts consisting of Al_2O_3 and MgO powders, close attention should be given to the intimacy of mixing. By employing a coprecipitation technique, desirable intimacy was achieved--giving rise to ready solid-state reaction and also high ultimate bulk density of the compact.

Further study will consist of microstructure examination, bulk density measurements, x-ray analysis, electron microscopy examination of sintered compacts of variable $\text{Al}_2\text{O}_3/\text{MgO}$ ratio in the spinel stability field.

Hopefully, some critical variables of the sintering process will be determined which may elucidate the role of solid solubility in the sintering of more complex ceramics systems.

1.8 Crystallization and Melting Kinetics in Glass-Forming Systems

Personnel: D. Uhlmann; P. J. Vergano

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

In glass-forming systems, measurement of crystallization and melting kinetics can be carried out over a wide range of temperatures. At the present time such measurements are being carried out on SiO_2 and GeO_2 .

In the case of germanium dioxide, measurements of crystal growth have been carried out in the temperature range between 700 and 1100°C ($T_E = 1115^\circ\text{C}$). In all cases, nucleation of the crystalline phase was observed to take place at the external surfaces; and crystallization proceeded by the propagation inward of the crystal-liquid interfaces. No internal nucleation of the crystalline phase was ever observed; and the interface morphology was found to be nonfaceted.

The growth rates, determined from the variation with time of the thickness of the external crystalline layers, were found to depend upon the atmosphere in which the crystallization is carried out, as well as upon the original melting conditions of the glass. Glasses of different water contents and states of reduction have been prepared by varying the melting conditions.

Combining growth rate with viscosity data on glasses prepared and tested under similar conditions, the reduced growth rate vs undercooling relation $(u\eta/[1-\exp(-\Delta h\Delta T/kTT_E)])$ was constructed. The form of this relation (a horizontal line over the full 400 degrees of undercooling) indicates an interface site factor which is independent of undercooling. The observed growth rates are higher by about a factor of 8 than those expected from the model of Wilson and Frenkel, using the Stokes-Einstein expression to relate the viscosity and the kinetic coefficient for transport at the interface.

Presently under study are the effect of stoichiometry on crystallization kinetics, as well as the kinetics of melting.

1.9 Crystallization and Melting Kinetics at High Pressure

Personnel: D. Uhlmann; T. J. Brown

Sponsorship: Atomic Energy Commission, Contract No. AT(30-1)-3773,
DSR 70112

The effect of high pressure on the kinetics of crystallization and melting are being investigated both theoretically and experimentally. The first materials being investigated experimentally include SiO_2 and B_2O_3 .

2.0 Relationship of Properties to Composition, Crystal Structure and Microstructure

Personnel: R. Coble, W. D. Kingery, B. J. Wuensch; H. T. Anderson, S. A. Cho, P. N. Dangel, T. R. Guillermo, I. Kohatsu, J. Conwicke, R. N. Katz, A. M. Mocellin, J. J. Rasmussen

2.1 Crystal Structure Studies

Personnel: B. J. Wuensch; H. T. Anderson, S. A. Cho, P. N. Dangel and T. R. Guillermo

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

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 which bears no obvious relationship to the structure of either end member in the system. Diffraction data have been obtained from crystals synthesized from As_3SbS_6 glass under 1000 bars pressure. The locations of the metal atoms in the unit cell have been determined. The phase is a layer structure which may be related to a highly distorted version of the atomic arrangement in 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 coordinates seems desirable.

2.1.2 Tetrahedral Phases

Personnel: B. J. Wuensch; P. N. Dangel

It has been possible to understand, in terms of valence electron concentration, the existence of over 200 phases in which the bonding occurs through sp^3 hybridization. These materials include many important semiconductors. A few exceptions to these rules exist. It has been proposed that either the compositions assigned to these phases, the crystal structures reported, or both, are incorrect. An example is a phase assigned composi-

tion $\text{Cu}_3(\text{As}, \text{Sn}, \text{V})\text{S}_4$ which had been reported as having the sphalerite structure. It has been found that supposed single crystals consist of an intergrowth of Sn-rich and Sn-poor phases. The Sn-containing phase has been shown to be a cubic super-structure based upon a sphalerite arrangement. Diffraction data have been collected. Derivative-structure theory has been used to show that 8 configurations are possible for the bulk of the atoms in the sphalerite array. Each of these possibilities is currently being tested.

The structure of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, previously supposed to be a tetrahedral compound, was determined earlier in this program. This phase may accept fairly large amounts of Hg in solid solution. This feature is of crystal-chemical interest in that Hg normally assumes an octahedral coordination, and no site of this type is occupied in the structure. A structure determination of a Hg-rich phase is in progress in an attempt to locate the position of Hg and thus identify the mechanism of solid solution.

2.1.3 Superstructures Based Upon the Rock Salt Arrangement

Personnel: B. J. Wuensch; S. A. Cho

Certain Pb-containing sulfides form complex superstructures based upon a rock salt-like array of atoms. Determination of a number of these superstructures is in progress in an attempt to determine the conditions under which such phases may form, and to understand why but a few of the many compositions are stable. The structures under investigation are those of $\text{Pb}_{13}\text{As}_7\text{S}_{23}$ which has

$$(a, b, c) = [1 \ 0 \ \bar{1} / \frac{10}{3} \ \frac{10}{3} \ \frac{10}{3} / 0 \ \bar{1} \ 1] (A_1, A_2, A_3)$$

and PbAgSbS_3 which has

$$(a, b, c) = [1 \ 1 \ 0 / \frac{3}{2} \ \frac{3}{2} \ 0 / 0 \ 0 \ 1] (A_1, A_2, A_3)$$

2.1.4 Vacancy Ordering and Ferrimagnetism in the System Fe-S

Personnel: B. J. Wuensch

The system Fe-S exhibits complex magnetic behavior which is still incompletely understood. Stoichiometric FeS is antiferromagnetic. Those with large departures from stoichiometry occur due to Fe vacancies in a NiAs-like structure. A number of superstructures exist in which the

the vacancies assume an ordered configuration. A crystal structure determination of an ordered monoclinic superstructure near composition Fe_7S_8 is continuing. Of particular interest is the relaxation of the structure in the vicinity of a vacancy.

2.1.5 Cation Distribution in Nonstoichiometric Spinels

Personnel: B. J. Wuensch; H. T. Anderson

A number of ceramic systems possess an intermediate phase XZ_2O_4 which has the spinel structure. The stability field of this phase commonly extends over wide ranges of stoichiometry towards Z_2O_3 at elevated temperatures. MgGa_2O_4 spinels have been synthesized and cation distributions are being determined as a function of the degree of nonstoichiometry. The possibility of vacancy ordering at high defect concentrations will be examined.

2.1.6 Structural Study of the Phase Transformation in CuAgS

Personnel: B. J. Wuensch; T. R. Guillermo

CuAgS exhibits an unusual phase transformation in the neighborhood of 100°C . The transformation involves an unusual 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 structure of both phases of CuAgS at several temperatures spanning the transformation. The resulting structural data will be used to relate changes of bond length with thermal expansion data, to study atomic vibrations near the transformation point, and to determine variations of site occupancies with temperature in the high-temperature phase.

2.2 Crystal Chemistry of Sulfosalts

Personnel: B. J. Wuensch; S. A. Cho, I. Kohatsu

Sponsorship: National Science Foundation, GA-1549; DSR 71042

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 and, because of formidable experimental problems

associated with their study, very few structures are known.

2.1 Bismuth Sulfosalts

The structure of aikinite, PbCuBiS_3 , is an interesting derivative of the structure of Bi_2S_3 : Pb substitutes for 1/2 of the Bi in the latter structure and Cu occupies a normally vacant tetrahedral interstice. The rough details of this structure are known, but the S positions are uncertain, and Pb and Bi were not distinguishable. The structure of aikinite has been confirmed, but refinement could not be carried to a point sufficient to permit distinction between Bi and Pb. New data are presently being obtained. Work has also been initiated on a series of more complex Pb-Cu bismuth sulfosalts. These phases are superstructures, based on aikinite, in which only a portion of the tetrahedral sites are occupied by Cu.

The primary tool for distinction between Pb and Bi (which have nearly identical scattering powers) 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.

2.2 Antimony Sulfosalts

Personnel: B. J. Wuensch; S. A. Cho

The system $\text{PbS-Sb}_2\text{S}_3$ contains at least 19 intermediate phases. None of their crystal structures are known. Curiously, there is little correspondence with the sequence of phases occurring in the system $\text{PbS-As}_2\text{S}_3$. Of particular interest is the plagionite group, an apparent homologous series $\text{Pb}_{3+2n}\text{Sb}_8\text{S}_{15+2n}$ in which two lattice dimensions remain invariant, while the third increases with n. A structure determination of plagionite, $\text{Pb}_5\text{Sb}_8\text{S}_{17}$ is in progress.

2.3 The Incorporation of Boron and Phosphorous in Vapor Deposited Beta-Silicon Carbide

Personnel: R. Coble; J. A. Conwicke

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

High purity and doped beta silicon carbide crystals were grown from

the vapor by the overall reaction $(\text{CH}_3)_2\text{SiCl(g)} \rightarrow \text{SiC(s)} + 3\text{HCl(g)}$. Transport in the gas phase appeared to be the rate-limiting step in the deposition process.

Boron and phosphorous were introduced in the crystals by diborane and phosphine gas additions to the feed stream. The amount of boron or phosphorous incorporated in crystals grown at 1650°C from a 0.4 mole percent methyltrichlorosilane nutrient showed linear dependences to the first power of the input diborane or phosphine partial pressures to maximum concentrations of about 10^{19} B/cc and 5×10^{18} P/cc, respectively.

Computer analyses indicated that under the experimental conditions, $\text{BH}_3(\text{g})$ and $\text{P}_2(\text{g})$ were the major equilibrium boron and phosphorous bearing vapor species. The amounts of boron or phosphorous incorporated in the crystals also showed first power dependencies on the equilibrium $\text{BH}_3(\text{g})$ or $\text{P}_2(\text{g})$ partial pressures calculated from the input partial pressures of diborane or phosphine, respectively.

The condition $K_i > K'_S > K_S$ is shown to be a reasonable model for the defect chemistry in beta-silicon carbide. The results of the doping experiments are expected from the model proposed (n_i estimated to be $10^{19}/\text{cc}$) if $\text{BH}_3(\text{g})$ governs the solution reaction for the boron incorporation and the input $\text{PH}_3(\text{g})$ partial pressure governs the solution reaction for phosphorous doping. It is proposed that the reaction $2\text{PH}_3(\text{g}) \rightarrow \text{P}_2(\text{g}) + 3\text{H}_2(\text{g})$ is limited by kinetics.

Anomalous density changes in the undoped crystals are caused by the appearance of free carbon in the deposit which would not be predicted under equilibrium conditions. Free carbon in the deposit is attributed to soot formation in the gas phase caused by polymerization of carbon bearing species during heating with subsequent incorporation in the deposit.

2.4 Dislocation Behavior in Fluorite Structure Compounds

Personnel: R. Coble; R. N. Katz

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

Studies are continuing on the behavior of dislocation in CaF_2 . The main aspect of this work has been to measure the stress-velocity relationship as a function of temperature for both screw and edge dislocations. It has been established that a fraction of the screw and edge dislocations are more mobile than edge dislocations. Measurements of the stress-velocity relationship in BaF_2 have been initiated in order to ascertain whether the above

behavior is unique to CaF_2 or is general to the alkaline earth fluorides. An investigation of the effect of two-valent impurities on the relative behavior of edge and screw dislocations in CaF_2 is planned. It is hoped that analysis of the temperature and impurity governed variation in the stress sensitivity for dislocation motion, plus activation volume data, will permit the elucidation of the drag mechanism controlling dislocation motion in these materials.

2.5 Dopant Influence on Properties of Polycrystalline Aluminum Oxide

Personnel: W. D. Kingery; A. Mocellin

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

Aluminum oxide powders both pure and magnesium or silicon doped have been prepared by recrystallization and calcination of alum. Samples are to be vacuum hot-pressed in a tungsten die and will subsequently be creep tested under Nabarro-Herring conditions. Seeded samples are also being cold pressed, sintered, and heat treated under varying conditions for secondary grain growth studies. Microhardness and transmission electron microscopy are expected to evidence any impurity segregations.

It is suspected that electrostatic or space-charge effects are important in controlling the equilibrium configuration of point defects and the solubility characteristics in the material, hence affecting some of its properties and more or less governing the kinetics of most solid state processes. Special attention is therefore being given to this question from both a theoretical point of view and a practical approach by trying to relate experimentally observed quantities to parameters such as potential profile or width of the space charge layer.

2.6 Effect of Dopants on the Defect Structure of Single Crystal Aluminum Oxide

Personnel: W. D. Kingery; J. J. Rasmussen

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

The solubility mechanisms of dopants in single crystal aluminum oxide were determined by studying the density changes and lattice parameter changes which were introduced by the dopants. Czochralsky grown rubies containing from 0.054 to 0.160 weight percent chromium oxide and

Czochralsky grown sapphires containing from 0.083 to 0.120 weight percent titanium dioxide were studied. Crystals were grown by the Verneuil technique from powders containing 250 to 1000 parts per million calcium, cobalt, magnesium, silicon and vanadium.

The density changes were determined by measuring the densities of the doped crystals and comparing them with the measured densities of undoped crystals. The densities were determined within 5×10^{-3} percent or better using a hydrostatic weighing technique. The lattice parameter shifts were measured using a step scanning goniometer technique. The shifts were determined within 0.25 percent or better.

The crystals may appear to be single phase when they actually contain fine particles of a second phase. These second phase particles have been shown to change the expected density of a crystal. Transmission electron microscopy can and must be used to examine apparently single phase crystals for the presence of a second phase which will usually alter the properties of the crystal.

Vanadium ions go into solution in aluminum oxide predominantly in the three plus valence state with a solubility limit greater than 500 parts per million. Silicon ions go into solution with the formation of aluminum vacancies to maintain charge neutrality. The solubility limit is greater than 270 parts per million silicon. The solubilities for vanadium and silicon ions are determined for crystals which solidified from melts containing up to 1000 parts per million of the dopant initially. The titanium ions in sapphire which is grown by pulling from the melt are present in both the three and four plus valence states. The presence of 340 parts per million calcium in alumina crystals produces a sufficient amount of second phase that the solubility mechanism cannot be determined by measuring changes in density. The apparent decomposition of magnesium oxide and cobalt oxide during the Verneuil growth of alumina crystals containing these compounds as dopants prevents the solubility mechanism from being determined.

3.0 Structure and Properties of Noncrystalline Solids

Personnel: C. J. Mogab, D. R. Uhlmann; R. G. Block, T. J. Brown, R. M. Hakim, W. T. Laughlin, J. Li

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

3.1 Growth Kinetics of Epitaxial SiC Films

Personnel: C. J. Mogab

Under certain conditions, single crystals of the cubic polytype of silicon carbide can be grown epitaxially on crystals of Si by direct carburization. Present studies are directed toward an understanding of the growth mechanisms and kinetics. Epitaxial films can be grown at temperatures as low as 850°C. Reflection electron diffraction patterns of very thin overgrowths demonstrate good epitaxy with no evidence of any polycrystallinity. Thicker films often show a single crystal pattern superimposed on a weak polycrystalline pattern of cubic SiC. This evidence suggests that at some critical thickness the epitaxial relation is lost probably in an effort to relieve stresses generated in the over-growth as a result of a nearly 20% lattice parameter mismatch between Si and β -SiC.

Preliminary kinetic data suggest that the growth-rate is diffusion limited. The interesting aspect of these data is that the observed growth rates are much higher than one would predict based on an extrapolation of the measured self-diffusion coefficients for one of the hexagonal polytypes of SiC.

3.2 Annealing Kinetics in Non-Crystalline SiC, Si and Ge

Personnel: C. J. Mogab; R. G. Block

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Silicon germanium and SiC are all semiconducting materials which can be obtained in a non-crystalline state by vapor deposition. These three materials all undergo an irreversible reduction of conductivity on annealing. The kinetics of this process in non-crystalline SiC has been found to obey a logarithmic rate law consistent with thermally activated processes distributed in activation energy. The annealing has been attributed to the annihilation of acceptor-like levels near the edge of the valence band which originate from potential fluctuations inherent in the structural disorder of the material.

Work is now underway to determine whether the kinetics of the conductivity annealing in non-crystalline Si and Ge follow the rate law observed for amorphous SiC. Thin films of Si deposited on Sapphire substrates by electron beam evaporation at room temperature, 10^{-7} torr and about 40 Å/sec have

exhibited non-crystalline electron diffraction patterns. A method has been devised by which 12 films may be deposited simultaneously in order to insure identical deposition conditions. Each set of 8 to 12 films will be deposited at a different rate in order to determine the dependence of the distribution in activation energy upon deposition rate and film density. Any work in which the substrate temperature would be varied would be conducted at temperatures below room temperature as this is proceeding in the direction of increasing disorder.

3.3 Flow and Relaxation Processes in Simple Glass-Forming Liquids

Personnel: D. Uhlmann; W. T. Laughlin

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70012

The phenomena of viscous flow, dielectric relaxation, and volume relaxation in simple glass-forming liquids are being investigated. Measurements of viscous flow in α -phenyl o-cresol, salol, o-terphenyl and glycerin have been carried out over the range of viscosity from 10 to 10^{14} poise, using both bending-beam and falling-sphere viscosimeters. For α -phenyl and salol, the $\log \eta$ vs $1/T$ relations were straight lines over the viscosity range from 10^5 poise to the glass transition region, while for glycerin and o-terphenyl, curvature was noted in this high viscosity region. In the case of glycerin, the form of the viscosity data is consistent with the predictions of the excess entropy model of Gibbs and his co-workers, and is not so well given by the predictions of free volume models; with o-terphenyl, the form is that of the WLF relation, but the constants are poorly represented by the standard values; while for α -phenyl and salol, the form of the data is inconsistent with the predictions of any of the standard models. Taken in toto, these results suggest that the flow behavior of even relatively simple liquids is more complex than envisaged by any of the usual treatments.

Measurements of the thermal expansion and heat capacity for each of these materials--in the liquid, glass and crystalline states--have been carried out and the results of these measurements have been used in considering the flow behavior.

Studies of volume relaxation in the vicinity of the glass transition are now being completed. Preliminary results indicate non-simple relaxation behavior for all the materials.

3.4 Effect of High Pressure on Glass

Personnel: D. Uhlmann; T. J. Brown

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

A number of glasses have been shown to undergo a permanent densification when subject to high pressure. The variation of this densification with composition, temperature, and pressure has been investigated in a number of simple silicate systems, with greatest attention being directed to $\text{Na}_2\text{O-SiO}_2$ glasses.

At a given temperature and pressure, the densification is observed to increase with increasing concentration of alkali, go through a maximum and then decrease with further increases of modifier. For a given composition and temperature, the densification was found to increase with increasing pressure; and for a given composition and pressure, to increase with increasing temperature. At the highest pressure used to date (about 65 kb) no saturation was found in the densification vs pressure curves; and no meaningful order could be discerned in the densification observed at a given temperature, pressure, and composition for different types of modifying cations.

The investigation is presently being extended to include studies at appreciably higher pressures, and studies of the kinetics of annealing of the densification.

3.5 Viscous Flow in Glass Forming Liquids

Personnel: D. Uhlmann; J. H. Li

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

A molecular theory for viscous flow in glass-forming liquids is being developed. This theory treats the jumps of molecules from the original potential wells to shifted potential wells as well as to adjacent potential wells. A single-step approach, using the concept of two independent sets of energy levels--one representing the energy levels for the shifted and adjacent potential wells--is used to treat the model. The flow equation obtained by the model can be simplified to the form of a simple exponential function. In principle, the activation energy for flow in the model can be calculated directly from the molecular interactions, although this has not yet been

attempted in detail. It is also possible to explain the stress dependence of the viscosity, as well as and to relate viscoelasticity and the elastic properties of the materials to their flow properties.

3.6 Flow of Glass at High Stress Levels

Personnel: D. Uhlmann; J. H. Li

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

The flow of glass-forming liquids at high stress levels has been investigated at length. The results of this investigation have demonstrated in the case of a homogeneous rubidium silicate glass that there is a critical stress above which the viscosity decreases with increasing stress and the material no longer behaves as a Newtonian fluid. Under the uniaxial tensile conditions, this critical stress is approximately independent of temperature near the glass transition region and is equal to 1.4×10^9 dynes/cm² for the rubidium silicate glass. Decreases in viscosity of an order of magnitude from the low-stress values have been observed.

In contrast with the results obtained on the homogeneous rubidium silicate glass, a phase-separated borosilicate glass showed no evidence of non-Newtonian behavior--even for stresses as large as 2.3×10^{10} dynes/cm² under a uniaxial tensile condition.

The effect of phase separation on the viscosity of glass-forming liquids was also investigated. In this study, the viscosity of a 0.14 Na₂O-0.86 SiO₂ glass was found to depend mainly upon the morphology of the separated phases. This was found to result in a viscosity which could increase with increasing temperature (in addition to time)--due to the completion of the separation into a large scale three-dimensionally interconnected submicrostructure at the high temperatures.

3.7 Rapid Quenching of Nonmetallic Materials

Personnel: D. Uhlmann; T. J. Brown

Sponsorship: Atomic Energy Commission; AT(30-1)-3773, DSR 70112

The technique of splat-cooling (rapid cooling by propelling a molten sample onto a cold substrate) is being used to study nonmetallic materials. Particular emphasis is being placed on obtaining materials as glasses which

cannot ordinarily be obtained in the amorphous solid state and on obtaining homogeneous glasses of materials which ordinarily are obtained in a phase-separated condition.

3.8 Strength of Glass

Personnel: D. Uhlmann; J. H. Li

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

The strength of some simple inorganic oxide glasses is being investigated. Variables include size, composition, submicrostructure, drawing conditions, temperature, and time.

3.9 Electrical Properties of Glasses

Personnel: D. Uhlmann; R. M. Hakim

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

Measurements have been carried out of D. C. conductivity and dielectric relaxation in a series of single alkali silicate glasses, as well as in a group of mixed alkali (Cs-Rb, Cs-K, Cs-Na and Cs-Li) silicates.

In the binary glasses, the measurements of conductivity have been related to electron microscopic observations. No evidence is found for sharp breaks in the conductivity vs composition relations previously reported by other workers. The dielectric loss peaks are broader than Debye peaks, and are asymmetrically broader on the high-frequency sides. The frequency at the peak of the loss curve shifts with temperature by an apparent activation energy close to that observed for D. C. conduction. More detailed analysis of the loss curves is presently being completed, as is analysis of the data on the mixed alkali glasses.

A study is also being carried out on the effects of submicrostructure on the electrical properties of As-I-Te and As-Se-Te glasses, crystals, and glass ceramics. Measurements of D. C. conductivity, Hall effect, and Seebeck effect have been carried out, and are being correlated with the results of electron microscopic observations.

3.10 Phase Separation and Properties of Glasses

Personnel: D. Uhlmann

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

The relation between phase separation and various properties of glasses is being investigated. Initial attention is being directed to density, elastic moduli and thermal expansion, as well as to the conductive properties of glasses.

An attempt is also being made to establish a relation between various structural models and the thermodynamic parameters relevant to phase separation.

4.0 Materials Synthesis and Preparation

Personnel: W. D. Kingery, B. J. Wuensch; H. T. Anderson, J. R. Booth, H. K. Bowen, P. N. Dangel

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112;
National Defense Education Act Fellowship

4.1.1 Freeze-dry Preparation of Mixed Oxides

Personnel: B. J. Wuensch; H. T. Anderson

Sponsorship: Atomic Energy Commission, AF(30-1)-3773, DSR 70112

An apparatus has been assembled for the preparation of mixed oxides of controlled stoichiometry and homogeneity. The procedure following consists of the spraying of an aqueous solution of salts of the desired cations into a cooled organic liquid, such as hexane, with which water is immiscible. The frozen droplets are removed, dried in vacuum, and subsequently calcined. Since initial salts have had no opportunity to segregate, the resultant oxide is extremely homogeneous. The technique has been successfully used to prepare spinels of various composition.

4.1.2 Chemical Vapor Transport

Personnel: B. J. Wuensch; P. N. Dangel

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112

Many materials may be reacted with a carrier substance to form a gaseous species. If the gaseous species is allowed to diffuse into a cooler region of the chamber, the reaction is reversed, and the material may be deposited in single-crystal form. This technique is an attractive procedure for the preparation of small, highly perfect single crystals suitable for diffraction studies, especially for materials with high-vapor pressure or phase transformations which would preclude crystal preparation of standard techniques. Transport of zinc sulfide by iodine in a closed system is being studied to permit insight into the kinetics of the process and the optimization of variables before proceeding to more complex systems. Perfect single crystals of ZnS of millimeter dimensions have been successfully synthesized.

4.2 Solid Solubilities in Alumina and Magnesia

Personnel: W. D. Kingery; J. R. Booth

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70012

A study has been initiated to investigate the extent and nature of solid solubility in single crystal Al_2O_3 and MgO . Solute containing single crystals will be grown by a temperature-gradient vapor-transport process.

4.3 Thermophysical Properties of Nonstoichiometric Materials in a Thermal Gradient

Personnel: W. D. Kingery; H. K. Bowen

Sponsorship: Atomic Energy Commission, AT(30-1)-3773, DSR 70112;
National Defense Education Act Fellowship

Wustite (FeO_{1-x}) has been selected for initial thermal gradient property studies. A wealth of isothermal thermodynamic data are available for this nonstoichiometric oxide which will allow a priori composition versus temperature predictions for a given oxygen partial pressure. Measurement of structure-sensitive properties will then allow empirical determination of the composition variation and property changes resulting from the thermal gradient. Further studies will include UO_{2+x} .

An integral part of the study of materials is the preparation of well

characterized samples, especially if intrinsic properties are to be measured. Various methods for the preparation of oxides have been surveyed; chemical transport vapor deposition was determined to be the most favorable method. Initial growth studies were made on wustite. A dynamic growth technique (involving flowing H_2/H_2O over $FeBr_2$ crystals to deposit "FeO" epitaxially on MgO) was difficult to control. A static growth method which involves an encapsulated system within two temperature zones is easier to monitor and will be used for wustite sample preparation. Presently, equipment is being assembled which will be capable of controlling the temperature zones to ± 0.2 degrees at $1000^\circ C$ to allow homogeneous deposition.

Theses:

- R. M. Hakim, "Electrical Properties of Ionic and Semiconducting Glasses," Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1968.
- D. S. Gelles, "The Amorphous to Crystalline Transition in Barium Titanate ($BaTiO_3$)," S. M. Thesis, Department of Metallurgy and Materials Science, January 1968.
- S. Prochazka, "Sintering Kinetics of Alumina by Surface Measurement," S. M. Thesis, Department of Metallurgy and Materials Science, June 1968.

Publications:

- W. D. Kingery, "Effect of Low Temperature Neutron Irradiation and $20-400^\circ C$ Annealing on the Density and Lattice Parameters of Aluminum Oxide and Magnesium Oxide," J. Nucl. Mater., 24, 21-33 (1967).
- D. J. Bromer and W. D. Kingery, "Flow of Polycrystalline Ice at Low Stresses and Small Strains," 39, (3), 1688-1691 (1968).
- B. Francois, R. Delmas, G. Cizeron and W. D. Kingery, "Inhibition du frittage par developpement d'une pression gazeuse dans les pores," Memoires Scientifiques Rev. Metallurg., 64 (12), 1079-1094 (1967).
- B. Francois and W. D. Kingery, "The Sintering of Crystalline Oxides: I, Densification and Microstructure Development in UO_2 ," in Sintering and Related Phenomena, C. G. Kuczynski, N. Hooton and C. Gibbon, Eds., Gordon and Breach, New York (December 1967).
- W. D. Kingery and B. Francois, "The Sintering of Crystalline Oxides," II, Interaction Between Grain Boundaries and Pores," in Sintering and Related Phenomena, C. G. Kuczynski, N. Hooton, and C. Gibbon,

- Eds., Gordon and Breach, New York (December 1967).
- C. J. Mogab and W. D. Kingery, "Preparation and Properties of Noncrystalline Silicon Carbide Films," *J. Appl. Phys.*, **39** (8), 3640-3645 (1968).
- T. P. Jones, R. L. Coble, and C. J. Mogab, "Defect Diffusion in Single Crystal Aluminum Oxide," *J. Am. Ceram. Soc.* (in press).
- S. K. Roy and R. L. Coble, "Solubilities of Magnesia, Titania, and Magnesium Titanate in Aluminum Oxide," *J. Am. Cer. Soc.*, **51** (1), 1-6 (1968).
- T. L. Francis and R. L. Coble, "Creep of Polycrystalline Silicon Carbide," *J. Am. Ceram. Soc.*, **51** (2), 115-116 (1968).
- G. A. Keig and R. L. Coble, "Mobility of Edge Dislocations in Single Crystal CaF_2 ," *J. Appl. Phys.* (in press).
- R. L. Coble, "Development of Microstructures in Ceramic Systems," Third International Materials Conference, University of California, (Berkeley, June 13-17, 1966), in *CERAMIC MICROSTRUCTURES*, R. M. Fulrath and J. A. Pask, Eds., Wiley Publishers, New York (1968).
- R. E. Mistler, and R. L. Coble, "Microstructural Variation Due to Fabrication," *J. Am. Ceram. Soc.*, **51** (4), 237 (1968).
- R. E. Mistler and R. L. Coble, "Comments on the Use of Log-Log Plots in Analyzing Grain Growth Data," *J. Am. Ceram. Soc.*, **51** (8), 472 (1968).
- T. K. Gupta and R. L. Coble, "Sintering of ZnO: I, Densification and Grain Growth," *J. Am. Ceram. Soc.* (in press).
- T. K. Gupta and R. L. Coble, "Sintering of ZnO: II, Density Decrease and Pore Growth During the Final Stage of the Process," *J. Am. Ceram. Soc.* (in press).
- R. L. Coble and N. M. Parikh, "Fracture in Polycrystalline Ceramics," *TREATISE ON FRACTURE* (to be published).
- R. L. Coble and T. K. Gupta, "Intermediate Stage Sintering: I, Lattice and Boundary Diffusion Models; II, Experimental Data," in *Sintering and Related Phenomena*, G. C. Kuczynski, N. Hooton and C. Gibbon, Eds., Gordon and Breach, New York (December 1967).
- R. L. Coble, "Theory of Hot Pressing," in *Sintering and Related Phenomena*, G. C. Kuczynski, N. Hootnn and C. Gibbon, Eds., Gordon and Breach, New York (December 1967).
- B. J. Wuensch, "Comparison of the Crystallography of McGovernite, Dixentie, and Hematolite," *Zeitschrift für Kristallographie*, **127** (in press).
- B. J. Wuensch and T. Vasilos, "Impurity Cation Diffusion in Magnesium

- Oxide," in Mass Transport in Oxides, Nat. Bur. Stand., Special Pub. 296, 95-102 (1968).
- D. R. Uhlmann and K. A. Jackson, "Frost Heave in Soils, the Influence of Particles on Solidification," in Physics of Snow and Ice, Hokkaido University, Sapporo, Japan, 1968, pp. 1361-1373.
- P. J. Vergano and D. R. Uhlmann, "Crystallization of Germanium Dioxide," VI International Symposium of the Reactivity of Solids, Schenectady, New York, August 1968 (in press).
- T. P. Seward, D. R. Uhlmann and D. Turnbull, "Phase Separation in the System BaO-SiO_2 ," J. Am. Ceram. Soc., 51, 278 (1968).
- R. R. Shaw and D. R. Uhlmann, "Subliquidus Immiscibility in Binary Alkali Borates," J. Am. Ceram. Soc., 51, 377 (1968).
- T. P. Seward, D. R. Uhlmann and D. Turnbull, "Development of Two-Phase Structures in Glasses, with Special Reference to the System BaO-SiO_2 ," J. Am. Ceram. Soc., 51, 634 (1968).

XIII. POLYMERS AND GLASSES 17313

Faculty:

D. R. Uhlmann, Assistant Professor, Metallurgy and Materials Science

Research Staff:

T. J. Brown, Engineering Assistant, Metallurgy and Materials Science

Graduate Students:

J. B. Park, Research Assistant

R. M. Kimmel, Research Assistant

P. C. Calvert, Research Assistant

Degrees Granted:

R. M. Kimmel, Sc. D., Materials Engineering, Mechanical Engineering,
September, 1968

Personnel who have left:

Dr. R. M. Kimmel (now at Celanese Corp., Summit, N. J.)

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75127

Research Report:

1.0 Effect of High Pressure on Amorphous Polymers

Personnel: Professor D. R. Uhlmann; R. M. Kimmel

The permanent changes produced in the properties of glass-forming amorphous polymers by various combinations of high pressure and temperature are being investigated, using a Bridgman-Anvil "squeezer" apparatus, a piston-cylinder solid medium press, and a 200,000 psi gas apparatus.

The material studied in most detail has been polymethyl methacrylate (PMMA). In this case, the change in density, specific heat, and relative thermodynamic stability resulting from treatment at pressures to 50 kilobars and temperatures to 245°C have been investigated. Increases in density of up to 1.5 percent in specific heat of up to 0.9 %, and in relative thermodynamic stability are observed following treatment in the glass transition region. Increases in density of up to 0.5 %, little or no change in

specific heat and relative thermodynamic stability result from treatment in the glassy state. Changes in properties after treatment in the glass transition region at low pressure followed by rapid compression to high pressure are found to depend upon the duration of treatment in the glass transition region.

The detailed structure of the specific heat versus temperature curves of densified PMMA is found to depend upon the nature of the pressure-temperature treatment. Minima, multiple peaks, and very large peaks are observed at various temperatures.

The kinetics of the annealing of densified polymers at one atmosphere and temperatures below the glass transition have also been characterized in detail. The resistance to annealing is correlated with the relative thermodynamic stability of the densified material.

2.0 Time Dependent Properties of Glass Forming Systems

Personnel: Professor D. R. Uhlmann; R. M. Kimmel

The general phenomenological treatment of relaxation processes has been surveyed. The analysis of Primak for calculating distributions of activation energies from kinetic data has been rederived, and its relationship to analyses in terms of distributions of relaxation times has been explored. The analysis has been applied to various time dependent properties of glass-forming materials. These property changes include volume relaxation, time dependent mechanical properties, and annealing of densified glasses; and the results obtained using this analysis are being related to various theories of the glassy state and glass transition phenomena.

To date, activation energy spectra have been calculated for volume relaxation of polystyrene, polyvinyl acetate, and glucose; for annealing of densified polymethyl methacrylate and fused silica; for recovery of hot stretched polystyrene; and for glassy state creep of polymethyl methacrylate.

The results have been compared with thermodynamic theories of the glass transition and with analogous data on inorganic glasses. Possible physical interpretations of the activation energy spectra have been considered.

3.0 Deformation of Amorphous and Crystalline Polymers

Personnel: Professor D. R. Uhlmann; J. B. Park

The deformation of amorphous and crystalline polymers is being investigated with particular emphasis being placed on understanding the cold flow phenomenon. In elucidating the relation between this phenomenon and the structure of the polymers, emphasis is being placed on studying the kinetics

of recovery of the deformation, as well as upon the deformation process itself.

In results obtained to date, samples of amorphous polycarbonate has been deformed to strains of the order of 50%. On annealing at temperatures near the glass transition and above, this deformation is observed to recover completely. On subsequent testing, the samples are characterized by smaller values of the modulus yield strength than the initial material. An energy spectrum characterizing the annealing process has been derived from the annealing kinetics. This spectrum is found to sharpen and shift to lower energies with increasing temperature, but to be relatively independent of the extent of strain. Corresponding studies of partly crystallized polycarbonate, as well as of polypropylene, polyethylene and nylon are presently being carried out.

4.0 Crystallization of Polymers Under Pressure

Personnel: Professor D. R. Uhlmann; P. C. Calvert

The crystallization of several polymers under high pressure has been found to result in an extended chain conformation. The origin of this morphology is being investigated, as are the changes in the properties of polymers crystallized under high pressure. Most studies are being carried out in a 200,000 psi gas apparatus and in a piston-cylinder solid medium press. The first materials being investigated include polyethylene, polypropylene, and nylon.

5.0 Crystallization and Properties of Polymers

Personnel: Professor D. R. Uhlmann; P. C. Calvert, T. J. Brown

The effect of crystallization conditions on the morphology and properties of crystalline polymers is being investigated. The materials being investigated initially include: polyethylene, polypropylene, and nylon. An optical hot stage which permits separate variation of the temperature gradient and the rate of growth has been constructed, and is being used for a direct observation of the crystallization process, as ancillary to the study of the relations between crystallization conditions, crystallization morphology and properties.

Thesis

R. M. Kimmel, "Effects of High Pressure on Amorphous Polymers"

Sc.D. Thesis, Department of Mechanical Engineering, September 1968.

XIV. X-RAY AND ELECTRON OPTICS LABORATORY

Faculty:

R. E. Ogilvie, Professor, Metallurgy

Research Staff:

A. Saffir, DMD, Post Doctoral Fellow

L. Sutfin, DDS, Post Doctoral Fellow

Graduate Students:

J. S. Duerr, Research Assistant and Graduate Student

W. K. Jones, Instructor and Graduate Student

C. Lyman, Instructor and Graduate Student

Support Staff:

J. Adario, Technician, Metallurgy

J. Herman, Technician, Metallurgy

Calestine Carney, Secretary, Metallurgy

Degrees Granted:

R. H. Frost, Met. E., Metallurgy, June 1968

Sponsorship:

National Aeronautics and Space Administration, NsG-496 (part),
DSR 74568

National Institute of Health, 1 Ro1 AP 00859-01S1, IL-11196

Office of Naval Research, Nonr-1841(32), DSR 77590

National Institute of Dental Research, DE-105, DSR 71066

1.0 Study of Metallic Meteorites

Personnel: J. S. Duerr

Sponsorship: Smithsonian Astrophysical Observatory

A considerable amount of work has been done on the role of pressure, temperature, and time on the formation of the Widmanstätten pattern found in metallic meteorites. A cooling model with low internal pressure has been

proposed for the development of this pattern. Martensite morphology and crystallography are being studied in metallic meteorites using the scanning and transmission electron microscopes. In addition, the plessite areas are being chemically analyzed with an electron microanalyzer which has been modified to allow quantitative analyses of low carbon levels (0.1%) in an iron matrix. Carbon concentration as high as 1% has been measured in plessite in a meteorite with a bulk carbon concentration of 0.03%.

2.0 High Resolution Electron Probe Microanalysis of Biological Specimen

Personnel: L. Sutfin

Sponsorship: National Institute of Dental Research; Office of Naval Research

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. Emphasis is being placed on light element detection, but other materials applications will also be possible.

3.0 Biological Applications of the Electron Microprobe

Personnel: A. Saffir

Sponsorship: National Institute of Dental Research; Office of Naval Research

We are developing methods to resolve interferences between elements in electron microprobe analysis due to multiple order x-ray diffraction. Our technique consists of a two channel pulse height analysis in which both interfering elements are analyzed simultaneously from the same detector. We are particularly interested in the phosphorus-fluorine interference which is a great problem in biology.

We are continuing our research on the relationship between diet and the microcomposition, microstructure and caries resistance of teeth. Of special importance is the structure of the dento-enamel interface, which we are studying by scanning electron microscopy.

Publications:

- J. S. Duerr and R. E. Ogilvie, "Microprobe Analysis of Carbon Concentration in Several Iron Meteorites", Proceedings of the 31st annual meeting of the Meteoritical Society, October 1968.
- R. E. Ogilvie, "Cooling Studies of Fe-Ni Sphrules from the Barringer Crater," Proceedings of the 31st annual meeting of the Meteoritical Society, October 1968.
- R. E. Ogilvie, "Quantitative Electron Microprobe Analysis", Progress in Analytical Chemistry (1968).

XV. NUCLEAR MATERIALS LABORATORY

Faculty:

T. O. Ziebold, Associate Professor of Nuclear Materials, Nuclear Engineering

Graduate Students:

F. Berte, Graduate Student
T. P. Hulick, 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

Support Staff:

J. Adario, Technician, Metallurgy
J. Herman, Technician, Metallurgy
Calestine Carney, Secretary, Metallurgy

Degrees Granted:

E. M. Miller, S.M., Nuclear Engineering, September 1968
H. F. Bowman, Ph.D., Nuclear Engineering, June 1968

Sponsorship:

National Aeronautics and Space Administration, NsG-496, DSR 74599
Office of Naval Research, N00014-67-A-0204-0013, DSR 70591
National Science Foundation, GK-1768, DSR 70588
Atomic Energy Commission (contract pending)

1.0 Microanalysis of Fracture Surfaces

Personnel: K. Ohmae

Sponsorship: Office of Naval Research

Selected fracture specimens from the Naval Research Laboratory (NRL) program on the effects of minor elements of the behavior of A302-B steel have been examined in the scanning electron microscope and the electron microprobe analyzer. The fracture surfaces are seen to include a

relatively high density of MnS inclusions, and copper appears to segregate preferentially with the sulfides. Most significant is the fact that we have, for the first time, developed a technique for observing the "chemical microstructure" of a fracture surface. The next immediate task is to examine fracture in irradiated samples.

2.0 Neutron Bombardment Hardening of Iron Alloys

Personnel: G. R. Odette

Sponsorship: Office of Naval Research

Various radiation damage models postulate that the radiation-induced increase in yield strength is a function of either the total number of displaced atoms, the number of depleted zones (large vacancy clusters), or the number of primary cascades above a critical size. The problem is obviously complex, as indicated by the observed dependence of hardening rate on impurity content and mechanical and thermal history, for example. The dependence on the neutron spectrum itself may be more complex than indicated by a single, dominant defect mechanism because the interaction of different types of defects may be an important variable. For example, a large thermal flux component might not produce significant hardening itself but it may introduce defects that stabilize other defects produced by higher energy neutrons.

In order to differentiate the damage models, comparison of experiment with theory must be made on the basis of accurately characterized primary knock-on atom (PKA) spectra. For the analytical part of this study the PKA spectra will be calculated with a minimum of approximations. The effects of nonelastic and nonisotropic scattering will be treated in detail. The models will be characterized on the basis of differential damage cross sections, or damage response functions. Calculation of these functions will be based on careful consideration of the primary introduction of the defects and their subsequent rearrangement and interaction with dislocations to produce hardening.

3.0 Proton Bombardment to Study (n, p) Reaction Effects in Iron

Personnel: E. M. Miller

Sponsorship: Office of Naval Research

This was a feasibility study to determine whether hydrogen implanted in iron by proton bombardment would form grain boundary bubbles or other observable defects. Although proton bombardment did significantly increase the surface hardness of iron foils, we were able to see any defects attributable to radiation by thin film transmission microscopy. We have no plans to continue this work at present.

4.0 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/cm² 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. Heat transfer from the sample as well as various safety parameters will be measured 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.

5.0 Microcracking in Welds of Nickel Base Alloys

Personnel: J. N. Lamb

Sponsorship: Atomic Energy Commission

The electron microprobe is being used to study the redistribution of alloy elements near fusion welds of nickel base alloys. Microcracking 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. Future work will be directed toward determining the effect of additions of impurity elements on the segregations of major alloy elements in this two-phase region.

Publications:

T. O. Ziebold, "Materials Engineering for Nuclear Power," Tech. Review, 70, 3-7 (April 1968).

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).

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:

- A. D. Chitaley, Research Assistant, Mechanical Engineering
- J. W. Carson, Research Assistant, Mechanical Engineering
- E. Dror, Research Assistant, Mechanical Engineering
- J. Joyce, Research Assistant, Mechanical Engineering
- R. Lotz, Research Assistant, Mechanical Engineering
- J. H. Williams, Research Assistant, Mechanical Engineering
- D. M. Tracey, Research Assistant, Mechanical Engineering
- I. F. Stowers, Research Assistant, Mechanical Engineering
- J. Friel, Undergraduate Assistant, Mechanical Engineering
- R. Harrington, Undergraduate Assistant, Mechanical Engineering
- R. Lee, 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)
- Rosi M. Gaudins, Secretary, Mechanical Engineering (part time)

Personnel who have left:

- A. D. Chitaley (Now at B. F. Goodrich Company, Cleveland, Ohio)
- R. Lotz (Now at the Department of Mechanical Engineering, MIT)
- J. H. Williams (Now at University of Cambridge, England)

Degrees Granted:

- A. D. Chitaley, Sc.D., Mechanical Engineering, June 1968
- J. W. Carson, S.M., Mechanical Engineering, September 1968
- J. A. Joyce, S.M., Mechanical Engineering, September 1968
- J. H. Williams, S.M., Mechanical Engineering, June 1968

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

Continued stereoscopic observations of ductile fracture with the scanning electron microscope have emphasized the importance of the zig-zag mode of crack growth, even in tension, and have shown the tendency of 45° shear cracks to fork toward the tensile flank. The growth of cracks under shear parallel to the leading edge of the crack may arise from such zig-zagging growth of holes from inclusions in transverse shear. Observations here on spall fractures produced in other laboratories show that in 6061-T6 aluminum there is a threshold stress above which other mechanisms than hole growth become important.

Optical stereomicrographs show that crack tips blunt only up to a point, after which they shear off in a pattern of sharp 90° grooves, whose growth has been predicted in some cases from slip line theory.

2.0 Analytical Results

In order to control the zig-zag mode of growth, families of asymmetrically grooved plane strain specimens have been designed for various amounts of triaxiality and kinds of slip fields. The slip line theory has been extended to predict the details of the low cycle fatigue crack growth in fully plastic bend specimens. It is currently being applied with success to the determination of flow fields around inclusions and holes subject to traction or displacement boundary conditions. Boundary conditions have been formulated for holes and inclusions in a regular lattice, taking advantage of the center of symmetry.

The solution for the steady state growth of cracks under longitudinal shear has provided a quantitative means for testing different fracture criteria against the ratios of applied stress for initiation and for unstable propagation.

3.0 Numerical Results

Solution of relevant problems involving notches and holes using available computer programs shows the need to specify tractions, displacements, or a relation between them at various points around the boundary. In high strength alloys, local strains in reasonably rounded grooves may reach 20% before the fully plastic stress field is attained, indicating the need for taking elastic strains into account. The development of solution techniques based on superpositions of dislocation stress fields has yielded good results in longitudinal shear, and has benefitted from allowing neighboring dislocations to cancel each other out, leaving much simpler flow fields. This work has also given insight into the connection between continuous arrays of dislocations and classical plasticity equations, indicating the relative rotation between element and crystal lattice that must be taken into account in developing a complete constitutive relation from continuum dislocation mechanics.

Theses:

- A. D. Chitaley, "Elastic-Plastic Mechanics of Cracks with Growth," Sc.D. Thesis, Department of Mechanical Engineering, June 1968.
- J. W. Carson, "Numerical Elastic-Plastic Analysis in Plane Strain," S.M. Thesis, Department of Mechanical Engineering, September 1968.
- J. A. Joyce, "Tensile Plastic Deformation at Notch Roots," S.M. Thesis, Department of Mechanical Engineering, September 1968.
- J. H. Williams, "Fracture Strains and Strain Hardening Correlations in Aluminum Alloys," S.M. Thesis, Department of Mechanical Engineering, June 1968.

Publications:

- J. E. Neimark, "The Fully Plastic, Plane, Strain Tension of a Notched Bar", J. Appl. Mech. 35, 111-116.
- F. A. McClintock, "Local Criteria for Ductile Fracture", Int. J. Fracture Mech. 4, 101-130, June 1968.
- F. A. McClintock, "A Criterion for Ductile Fracture by the Growth of Holes", J. Appl. Mech. 35, 363-371 (1968).
- F. A. McClintock, "On the Mechanics of Fracture from Inclusions", Ductility, ASM, 255-277 (1968).
- H. W. Huff, J. A. Joyce, and F. A. McClintock, "Fully Plastic Crack Growth under Monotonic and Repeated Bending", Sec. Int. Conf. on Fracture, Sussex (1969).

II. PLASTIC DEFORMATION AND STRAIN HARDENING

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Research Staff:

A. P. Tanon, Visiting Engineering, Mechanical Engineering

Graduate Students:

G. H. East, Research Assistant, Mechanical Engineering

J. A. Godrick, Research Assistant, Mechanical Engineering

W. Wu, Research Assistant, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering

Sandramarie Williams, Secretary, Mechanical Engineering

Jane Cummings, Secretary, Mechanical Engineering

Sponsorship:

National Science Foundation Grants GK-596, DSR 76044, and GK-3700

DSR 71350

Research Report:

The statistical theory for easy glide in pure face centered cubic metals which was described in last year's report has been re-examined and modified. It was recognized that in the mutual capture of segmented edge dislocations passing pairs of segments can tear away their neighboring captured segments as they bow out unless these neighboring segments are bound to their opposing numbers within a binding distance. Taking account of this neighboring segment interaction in the rates of dislocation capture, source formation, and source inactivation, it was found that the calculated rates of dislocation multiplication and strain hardening are very nearly equal to the experimentally observed rates under the best conditions of easy glide.

To extend the theory to explain changes of hardening rate upon strain rate and temperature changes, and to account for the well known size and shape effects, it is essential that the mechanism of hardening of secondary

slip systems be better understood. Such experiments are now in progress.

Experimental work has also begun on the study of strain hardening in tungsten single crystals in the temperature range 77° - 800° . Of special interest are the very high rates of strain hardening, the strain dependence of the strain rate sensitivity, the prominent unloading yield phenomena and the mechanism of the temperature dependence of the flow stress in the high temperature range.

Publications:

- A. S. Argon and W. T. Brydges, "Deformation of Copper in Easy Glide," *Phil. Mag.*, 18, 817 (1968).
- A. S. Argon and W. T. Brydges, "Deformation of Copper in Easy Glide," *Trans. Japan Inst. Metals*, 9, 756 (1968).
- A. S. Argon and G. East, "A Statistical Theory for Easy Glide," *Trans. Japan Inst. Metals*, 9, 757 (1968).
- A. S. Argon, "A Statistical Theory for Easy Glide II," in *Physics of Strength and Plasticity*, A. S. Argon, Editor, MIT Press, in press.
- A. S. Argon, "Dislocation Dynamics," *Materials Science and Engineering*, 3, 24 (1968).
- A. S. Argon, R. D. Andrews, J. A. Godrick and W. Whitney, "Plastic Deformation Bands in Glassy Polystyrene," *J. Appl. Phys.* 39, 1899 (1968).
- A. S. Argon, "Delayed Elasticity in Inorganic Glasses," *J. Appl. Phys.* 39, 4080 (1968).

III. MECHANISMS OF FATIGUE DAMAGE IN SEMI-BRITTLE MATERIALS AT ELEVATED TEMPERATURES

Faculty:

A. S. Argon, Professor, Mechanical Engineering

Graduate Students:

G. R. Cohen, Research Assistant, Mechanical Engineering
G. H. East, Research Assistant, Mechanical Engineering
J. A. Godrick, Research Assistant, Mechanical Engineering
Y. A. Patel, Research Assistant, Mechanical Engineering
R. N. Wright, NSF Fellow and Research Assistant, Metallurgy
and Materials Science
D. H. Hunt, Undergraduate, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker Mechanical Engineering
Sandramarie G. Williams, Secretary, Mechanical Engineering
Jane Cummings, Secretary, Mechanical Engineering

Personnel who have left:

G. R. Cohen (now Standard Pressed Steel Co., Jenkintown, Pa.)
J. A. Godrick (now Ledgemont Laboratory, Kennecott Copper Corp.,
Lexington, Mass.)

Degrees Granted:

G. R. Cohen, SM. Mechanical Engineering, January, 1969
J. A. Godrick, Ph.D. Mechanical Engineering, June, 1968
R. N. Wright, Sc.D. Metallurgy, January, 1969

Sponsorship:

National Science Foundation, GK-596, DSR 76044
Advanced Research Projects Agency, SD-90, DSR 75109

Research Report

When lithium fluoride is cycled below 400° C. it rapidly strain hardens and does not fatigue. In a Prot type test it undergoes brittle

cleavage fracture in one cycle when the stress becomes large enough. Above 400°C . where both dislocation climb and cross slip are rapid, the crystals fatigue by a continuous process of volume degradation, first discernible by developing opacity. Investigations by light microscopy of the interior of the crystals and by scanning electron microscopy of cleavage surfaces reveals that cycling develops porosity which accumulates at deformation induced boundaries where cracks are eventually produced. Fatigue experiments on silver chloride where similar damage occurs above 150°C . indicate that the requisite of this type of damage is a temperature high enough for both dislocation climb and large scale cross slip to occur freely.

Further experiments on aluminium oxide are now in progress.

Fatigue crack propagation in Iron - 3% silicon alloy was studied at temperatures above room temperature. Above 150°C . the crack propagation rate obtained by measuring the changing compliance of the specimen is proportional to the second power of the stress intensity factor based on the stress range and is practically uninfluenced by the maximum stress. Although the crack propagation rate based on fracture surface striations has the same dependence on the stress range, its magnitude is 4-5 times larger than the macroscopic rate. The features of the fracture surface and the profiles of cracks indicate that the actual crack propagation involves stages of steady propagation and stages of large scale blunting after which the local crack growth ceases for many cycles. Although the rates of crack propagation and the fracture surface features favor a purely ductile crack growth by accumulation of irreversible distortions, the extreme roughness of the fracture surface and the large local departures of the crack plane from the average crack plane leave many questions to be answered.

Below 150°C . the crack propagation has a cleavage component which strongly increases the rate of crack propagation.

Experiments are in progress to study the development of fatigue damage in transparent glass-silver chloride composite materials.

Theses:

- G. R. Cohen, "Fatigue of Silver Chloride", SM Thesis, Department of Mechanical Engineering, Sept., 1968
- J. A. Godrick, "Fatigue Damage in Lithium Fluoride at Elevated Temperatures", Ph.D. Thesis, Mechanical Engineering, June, 1968
- R. N. Wright, "Fatigue Crack Propagation in Iron-Silicon", Sc.D. Thesis, Metallurgy, Oct., 1968

Publications:

- A. S. Argon and J. A. Godrick, "Fatigue of Lithium Fluoride Crystals at Elevated Temperatures", Czech. J. Phys., in the press.
- A. S. Argon and J. A. Godrick, "Fatigue of Lithium Fluoride Crystals at Elevated Temperatures", to be presented at the Second International Conference on Fracture at Brighton, England in April, 1969.

IV. INVESTIGATIONS OF MECHANICS AND PHYSICS OF DAMAGE IN HETEROGENEOUS MATERIALS

Faculty:

C. A. Berg, Associate Professor, Mechanical Engineering

Graduate Students:

A. Lew, Research Assistant, Mechanical Engineering

R. Hamilton, NSF Fellow, Mechanical Engineering

Support Staff:

W. Henry, Instrument Maker, Mechanical Engineering

P. Beecher, Secretary, Mechanical Engineering

Sponsorship:

Advanced Research Projects Agency, SD-90, DSR 75110

Research Report:

Experimental studies of cracking in transparent composite materials has begun, by using notched specimens of epoxy resin reinforced with glass rods as scaled up versions of fibre reinforced composite. The details of deformation about a notch tip are being observed with an optical microscope, as well as the process of initiation of damage in the vicinity of the notch tip.

The deformation prior to initiation of fracture is observed to determine the extent to which the displacement and strain field near the notched tip, where high strain gradients make the effect of material heterogeneity most important, depart from those indicated by classical calculations which neglect material micro-heterogeneity. The observations should indicate the extent to which long range spatial correlations in mechanical behavior, introduced by the micro-heterogeneity and the large strain gradients, influence the displacement field about the notch tip; one wishes to determine whether classical (micro-homogeneous) models of the material provide a sufficiently accurate description of the displacement field near the notch, and if not, what additions to the classical mechanical description of the material are required to yield an adequate representation. Since there has been considerable theoretical speculation on this point, without a definite result having emerged, the question is being studied here by direct experi-

mentation.

The damage initiation process cracking in advance of the notch tip preceding notch extension is observed to determine the initial sources of damage and the stochastic character of initial damage. Theoretical studies of the statistics of damage initiation in front of a notch tip will also be undertaken.

V. PROPERTIES OF FIBER COMPOSITES

Faculty:

J. Wulff, Professor, Class of 1922 Emeritus, Metallurgy and
Materials Science

J. W. Mar, Professor, Aeronautics and Astronautics

Research Staff:

L. A. Shepard, Research Associate, Metallurgy and Materials Science

Graduate Students:

G. O. Garmong, Graduate Student, Metallurgy and Materials Science

S. Weidenshilling, Graduate Student, Aeronautics and Astronautics

D. A. White, Graduate Student, Naval Architecture

P. Dickenson, Graduate Student, Naval Architecture

Degrees Granted:

P. W. Heitman, Ph.D., Metallurgy and Materials Science,
September 1968

R. W. Render, S.M., Naval Architecture, June 1968

H. C. Lewis, S.M., Naval Architecture, June 1968

W. L. Marsh, S.M., Naval Architecture, June 1968

Sponsorship:

Air Force Office of Scientific Research, AF 49(638)-1463

Research Report1.0 Directionally Solidified Eutectic Fiber Composites

Tensile properties of Al-Al₃Ni eutectic fiber composites were studied from room temperature to 600°C (0.95 T_m) over three orders of magnitude in strain rate and fiber spacings from 1.5 to 2.5 microns. Strain rate and fiber spacing effect were small compared with those due to fiber denuded grain boundaries and fiber orientation spread. Average values of tensile strength for samples with few grains and good fiber alignment considerably exceed the best commercial aluminum alloys above 300°C, decreasing from 21000 psi at 300°C to 4000 psi at 600°C.

2.0 The Effect of Fiber-Matrix Reaction and Compound Formation on Composite Strength and Fracture

For aluminum-molybdenum fiber composites with brittle fiber interface compound, if the filament is ductile and notch insensitive, composite strength may be predicted from a modified mixture rule neglecting the compound strength contribution. For notch sensitive filaments, severe strength degradation occurs with less than 1% compound. Ten percent compound results in a 50% strength decrease, but larger amounts of compound cause little further reduction. For low compound fractions, composite failure occurs by a statistical accumulation of fiber breaks.

3.0 The Strengthening Effect of Small Matrix Spacing in Fiber Composites

Cu-Fe composites with iron fiber diameters and copper matrix spacings from 250 microns to 0.25 microns and fiber volume fractions from 6% to 85% were fabricated by the bundle and draw method. Completely recrystallized samples were tested in tension over temperatures from 77°K to 373°K, providing a range of relative strength values for the two components.

Maximum composite strength is found at intermediate fiber volume fractions with fiber and matrix dimensions in the 0.25 micron range. These composites exceed the strength of recrystallized iron wire, even when grain size effects are taken into account.

Theses:

- P. W. Heitman, "Fracture of a Molybdenum-Aluminum Fiber Composite", Ph. D. Thesis, Department of Metallurgy and Materials Science, September 1968.
- R. W. Render, "Temperature and Strain Rate Dependence of Deformation in Al_3Ni -Al Composites", S. M. Thesis, Department of Naval Architecture, June 1968.
- H. C. Lewis, "Effect of Interfiber Spacing on the High Temperature Deformation of Al- Al_3Ni Composites", S. M. Thesis, Department of Naval Architecture, June 1968.
- W. L. March, "Production of Plates of Fiber Composites by Solidification and Hot Press Lamination", S. M. Thesis, Department of Naval Architecture, June 1968.

VI. PHYSICAL AND CHEMICAL PROPERTIES OF FIBERS AND
POLYMERS

Faculty:

S. Backer, Professor, Mechanical Engineering
I. V. Yannas, Assistant Professor, Mechanical Engineering
E. S. Gilfillan, Visiting Professor, Mechanical Engineering

Research Staff:

E. I. Valko, Senior Research Associate, Mechanical Engineering
H. U. Rudolf, Research Associate, Mechanical Engineering
R. C. Sheldon, Instructor, Mechanical Engineering
Miriam Chu, DSR Staff, Mechanical Engineering
S. Dayhoff, DSR Staff, Mechanical Engineering

Graduate Students:

R. M. Kimmel, Research Assistant, Mechanical Engineering
F. DeS. Lynch, Graduate Student, Mechanical Engineering
H. R. Plonsker, Graduate Student, Mechanical Engineering
E. C. Ibe, Graduate Student, Mechanical Engineering
A. Maranci, Graduate Student, Mechanical Engineering
S. C. Dangel, Graduate Student, Mechanical Engineering
N-H. Sung, Graduate Student, Mechanical Engineering
S. Arghyros, Graduate Student, Mechanical Engineering
H. Patel, Graduate Student, Mechanical Engineering
D. Jilla, Graduate Student, Mechanical Engineering
D. Rice, Graduate Student, Mechanical Engineering
A. Crugnola, Graduate Student, Mechanical Engineering
A. Lunn, Graduate Student, Mechanical Engineering
R. Naar, Graduate Student, Mechanical Engineering
A. Eltayebi, Graduate Student, Mechanical Engineering
A. Shiekh, Graduate Student, Chemical Engineering
J. Shah, Graduate Student, Mechanical Engineering
T. Suraiya, Graduate Student, Mechanical Engineering

Support Staff:

Dorothy Eastman, Secretary, Mechanical Engineering
Consuelo Godfrey, Secretary, Mechanical Engineering

Degrees Granted:

H. R. Plonsker, Sc.D., Mechanical Engineering, February 1968
F. DeS. Lynch, Sc.D., Mechanical Engineering, February 1968
R. M. Kimmel, Sc.D., Mechanical Engineering, September 1968
D. A. Jilla, M.S., Textile Technology, September 1968
N. Jain, M.S., Textile Technology, September 1968

Sponsorship:

Allied Chemical Corporation
Beaunit Corporation
Burlington Industries, Inc.
Department of Commerce, NBS CST-164, DSR 76268
Derby Foundation
E. I. duPont de Nemours & Co., Inc.
Camille and Henry Dreyfus Foundation
Instron Corporation
Charles T. Main Company
Maremont Foundation (Saco Lowell)
Monsanto Corporation
National Institutes of Health, 1-R01-AM11919-01, DSR 71218
National Science Foundation, GK-2024, DSR 70976
Phillips Petroleum Company
J. P. Stevens Company
West Virginia Pulp and Paper Corporation

Research Report**1.0 Bending Mechanisms in Textile Structures**

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, H. U. Rudolf, M. L. Chu, R. A. Roach, S. Dayhoff

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. Current efforts are directed towards building up a store for an extensive industry-cooperative experiment early in 1969.

3.0 Nonlinear Viscoelastic Behavior of Polymers

Personnel: I. Yannas, A. Lunn, N. Sung, S. Kornfeld, J. Shah

17314

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

17315

The isothermal relaxation of birefringence in polycarbonate and other synthetic polymers is under investigation.

6.0 Heat Setting of Nylon 6.6

Personnel: S. Backer; 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.

17316

7.0 Direct Conversion of Chemical to Mechanical Energy

17317 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 Differential Distribution of Crosslinks in Cotton

17318 Personnel: E. I. Valko, H. U. Rudolf

Experiments are carried out to control the differential distribution of crosslinks in cotton fibers by application of the crosslinkers from solvents.

9.0 Diffusion in Crosslinked Cellulose

17319 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 on polymers in general.

10.0 Theory of Dyeing Synthetic Polymers

17320 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:

H. R. Plonsker, "The Dynamics of Roller Drafting", Sc.D. Thesis, Department of Mechanical Engineering, February 1968.

F. DeS. Lynch, "A Finite Element Method of Viscoelastic Stress Analysis with Application to Rolling Contact Problems", Sc.D. Thesis, Department of Mechanical Engineering, February 1968.

- R. M. Kimmel, "Effects of High Pressure on Amorphous Polymers",
Sc.D. Thesis, Department of Mechanical Engineering, September
1968.
- N. K. Jain, "Annealing of Internal Stresses in Amorphous Polycarbonate",
M.S. Thesis, Department of Mechanical Engineering, September
1968.
- D. A. Jilla, "Hysteresis in Textile Bending", M.S. Thesis, Department of
Mechanical Engineering, September 1968.
- P. M. Jacobs, "Reaction of Cellulose Acetate with Ethyleneimine", M.S.
Thesis, Department of Mechanical Engineering, June 1968.

Publications:

- R. C. Sheldon, R. A. Roach, and S. Backer, "Design of an On-Line
Computer Based Textile Information Retrieval System," Textile
Research Journal 38, 81-100 (1968).
- R. D. Wells, "Pattern of Flow of Technical Information--A Design
Problem for the Textile Industry," Textile Research Journal 38,
332-338 (1968).
- S. Backer, R. C. Sheldon, and R. A. Roach, "Information Storage and
Retrieval by Electronic Data Processing," American Association for
Textile Technology Technical Review and Register, 28-38 (1968).
- S. Backer, R. C. Sheldon, and R. A. Roach, "Computer Storage and
Retrieval of Apparel Information," Bobbin Magazine, to be
published.
- 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 (in press).
- S. Backer and E. I. Valko, Thesaurus of Textile Terms, 2nd Edition,
MIT Press, Cambridge, Massachusetts, January 1969.
- S. Backer, J. W. S. Hearle, and P. Grosberg, "Structural Mechanics of
Fibrous Materials," Interscience Publishers, New York, New York
(in press).
- C. J. Monego and S. Backer, "Tensile Rupture of Blended Yarns,"
Textile Research Journal 38, 762-766 (1968).
- P. Popper and S. Backer, "Instrument for Measuring Bending-Moment
Curvature Relationships in Textile Materials," Textile Research
Journal 38, 870-873 (1968).
- 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, U. S. Patent #3,390,009, June 25, 1968. Process Rendering Hydrophobic Fibers Containing Textile Antistatic and the Treating Composition.
- I. V. Yannas, "Vitrification Temperature of Water," Science 160, 298-299 (1968).
- I. V. Yannas, A. V. Tobolsky, "High Temperature Transformations of Gelatin," European Polymer Journal 4, 257-264 (1968).
- I. V. Yannas, "Isochronal Temperature--Concentration Diagram for a Polymer-Diluent System," J. Polymer Science, Part A-2, 6, 687-694 (1968).
- I. V. Yannas and A. V. Tobolsky, "Stress Relaxation of Anhydrous Gelatin Rubbers," J. Applied Polymer Science 12, 1-8 (1968).

VII. STRUCTURAL MATERIALS

Faculty:

- F. J. McGarry, Professor, Civil Engineering
- R. C. Jones, Associate Professor, Civil Engineering
- F. Moavenzadeh, Associate Professor, Civil Engineering
- R. B. Williamson, Assistant Professor, Civil Engineering

Research Staff:

- C. B. Arends, Visiting Scientist, Civil Engineering
- M. H. Gradowczyk, Research Associate, Civil Engineering
- L. Szekessy, Research Engineer, Civil Engineering
- A. M. Willner, Instructor, Civil Engineering
- A. J. O'Neill, Technical Instructor, Civil Engineering

Graduate Students:

- J. A. Alexander, Research Assistant, Civil Engineering
- T. W. Bremner, Research Assistant, Civil Engineering
- C. B. Doughty, Research Assistant, Civil Engineering
- J. F. Elliott, Research Assistant, Civil Engineering
- G. Farra, Research Assistant, Civil Engineering
- P. Forroton-Rad, Research Assistant, Civil Engineering
- K. E. Fusch, Graduate Student, Civil Engineering
- R. C. Laible, Graduate Student, Civil Engineering
- F. V. Lawrence, Jr., Graduate Student, Civil Engineering
- A. C. Lemer, Research Assistant, Civil Engineering
- D. J. MacFadyen, Graduate Student, Civil Engineering
- A. J. Mancera, Graduate Student, Civil Engineering
- E. F. Olster, Research Assistant, Civil Engineering
- J. P. Scott, 3d, Graduate Student, Civil Engineering
- J. E. Soussou, Research Assistant, Civil Engineering
- J. N. Sultan, Research Engineer, Civil Engineering
- E. Tazawa, Graduate Student, Civil Engineering
- J. L. Walkinshaw, Graduate Student, Civil Engineering
- W. H. Everett, Northeastern University Cooperative Student, Civil Engineering
- M. Kupferman, Northeastern University Cooperative Student, Civil Engineering

- W. R. Navin, Northeastern University Cooperative Student, Civil Engineering
- N. S. Peterson, Northeastern University Cooperative Student, Civil Engineering
- R. F. Quinn, Northeastern University Cooperative Student, Civil Engineering
- J. Williams, Northeastern University Cooperative Student, Civil Engineering

Support Staff:

- J. T. King, Technician, Civil Engineering
- A. P. Rudolph, Jr., Machinist, Civil Engineering
- R. E. Boyd, Administrative Assistant, Civil Engineering
- Mary V. Dailey, Language Assistant, Civil Engineering
- Laura H. Eanes, Language Assistant, Civil Engineering
- Linda M. Gray, Language Assistant, Civil Engineering
- Bernadette Revest, Secretary, Civil Engineering
- Cynthia I. Sorenson, Secretary, Civil Engineering
- Marianne N. Stewart, Secretary, Civil Engineering

Degrees Granted:

- J. A. Alexander, S.M., Civil Engineering, September 1968
- C. B. Doughty, S.M., Civil Engineering, June 1968
- P. Forooton-Rad, C.E., Civil Engineering, June 1968
- K. E. Fusch, S.M., Civil Engineering, June 1968
- F. V. Lawrence, Jr., Sc.D., Civil Engineering, June 1968
- A. C. Lemer, S.M., Civil Engineering, June 1968
- D. J. Mac Fadyen, S.M., Civil Engineering, February 1968
- A. J. Mancera, S.M., Civil Engineering, February 1968
- E. F. Olster, S.M., Civil Engineering, February 1968
- J. E. Soussou, S.M., Civil Engineering, June 1968
- J. N. Sultan, S.M., Civil Engineering, February 1968
- E. Tazawa, S.M., Civil Engineering, February 1968
- A. M. Willner, Ph.D., Civil Engineering, February 1968

Sponsorship:

Listed under subheadings.

Research Report1.0 Brittle Fracture in Rocks and Portland Cement Concrete1.1 Brittle Fracture in Rock

Personnel: F. J. McGarry, R. B. Williamson and F. Moavenzadeh;
P. Forootan-Rad, G. Farra, C. R. Nelson, and A. C. Lemer

Sponsorship: U. S. Department of Transportation, Northeast Corridor
Transportation Project, C85-65, DSR 76103

The purpose of this study is to find physical or chemical means of reducing the energy and maximum stress necessary to fracture rock materials. Fracture surface work values have been measured for granite, marble, gneiss and schist using a stable cracking flexural test. Load-deflection curves have been recorded and the work expended to cause failure has been calculated. The extent of side cracking has been measured by quantitative microscopy and is used to calculate a corrected fracture work.

The addition of dilute aqueous solutions of surface active agents and certain salts has been found effective in decreasing both the maximum stress and the total work necessary to fracture the sample. A one percent aqueous solution of aluminum chloride at 90°C produces a fifty percent reduction in the fracture surface work, compared to the room temperature dry condition.

Thermal cycling of standard samples of each of the rocks is found to cause extensive cracking, and the resulting decrease in strength can be measured. The heat treatments are given at 540°C, 1280°C and 1800°C for one, five and ten cycles. Generally, the first heating cycle accomplished a major portion of the damage.

A 1000-watt continuous operation CO₂-N-He gas laser has been employed to subject the rock samples to high fluxes of infrared radiation. This substantially weakens the rock after a few seconds of exposure. Extensive macroscopic cracks have been observed after thirty to sixty seconds of irradiation.

Related Academic Subjects

- 1.41 Strength of Structural Materials
- 1.46 Portland Cement Concrete

Theses:

- P. Forootan-Rad, "Crack Initiation and Propagation in Rock," C. E. Thesis, Department of Civil Engineering, June 1968.
- A. C. Lemer, "Chemical Effects on Creep and Long Term Rupture in Rocks," S.M. Thesis, Department of Civil Engineering, June 1968.

Publications:

- F. Moavenzadeh, R. B. Williamson and F. J. McGarry, "Thin Disk Technique for Analyzing Rock Fractures Induced by Laser Irradiation," Publication R68-21, Civil Engineering, MIT, May 1968.
- P. Forootan-Rad and F. Moavenzadeh, "Crack Initiation and Propagation in Rock," Publication R68-29, Civil Engineering, MIT, May 1968.
- R. B. Williamson, F. Moavenzadeh and F. J. McGarry, "Some Relationships between Power Level, Exposure Time, Sample Size and Weakening in Laser-Assisted Rock Fracture," Publication R68-30, Civil Engineering, MIT, May 1968.
- A. C. Lemer, "Chemical Effects on Creep and Long Term Rupture in Rocks," Publication R68-31, Civil Engineering, MIT, May 1968.
- F. J. McGarry, R. B. Williamson and F. Moavenzadeh, "Laser Assisted Rock Fracture," Proceedings, Twelfth South American Meeting of Structural Engineering, Third Pan American Symposium of Structures, Fifth Technical Session, Caracas, Venezuela, July 7, 1967.
- R. B. Williamson, F. Moavenzadeh and F. J. McGarry, "Laser Assisted and Chemically Assisted Rock Fracture," Proceedings, Ninth Congress, International Bureau for Rock Mechanics, Leipzig, Germany, October 1967 (in German).
- F. J. McGarry, R. B. Williamson and F. Moavenzadeh, "Rock Fracture by Laser Irradiation," Proceedings, American Institute of Chemical Engineers Materials Conference, Philadelphia, Pa., April 1968.
- F. J. McGarry, "Underground Tunnels for Transport System", Proceedings of the Institute of Electrical and Electronic Engineers, Vol. 56, No. 4, 535, April 1968 (Special Issue on TRANSPORTATION).

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, Texas, September 29-October 2, 1968.

1.2 Brittle Fracture in Concrete

Personnel: F. Moavenzadeh; R. Kuguel, A. J. Mancera, T. W. Bremner, J. E. Soussou

Sponsorship: Ford Foundation, DSR 76393

The purpose of this study is to provide a fundamental knowledge of the mechanism of fracture of brittle materials and its application to the understanding of the strength of portland cement concrete. It is anticipated that such a study will eventually lead to the development of a more rational method of design of concrete structures, and to the manufacture of better quality concrete.

Related Academic Subjects

- 1.40 Introduction to Electron Microscopy
- 1.41 Strength of Structural Materials
- 1.44 Cementitious Materials
- 1.46 Portland Cement Concrete

Publications:

- F. Moavenzadeh, R. Kuguel and L. B. Keat, "Fracture of Concrete," Publication R68-5, Civil Engineering, MIT, March 15, 1968.
- A. J. Mancera and R. B. Williamson, "The Microstructure and Mechanical Properties of the Portland Cement-Slag System," Publication R68-32, Civil Engineering, MIT, May 1968.
- F. Moavenzadeh, "Application of Systems Methodology to the Concrete Industry," (Term Projects in 1.46, Concrete Technology), Publication R68-64, Civil Engineering, MIT, June 1968.

✓ 2.0 The Solidification of Crystalline Polymers

17321

Personnel: R. B. Williamson and F. J. McGarry; C. B. Doughty,
J. N. Sultan, A. M. Willner

Sponsorship: Manufacturing Chemists' Association, Inc., 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
- 1.471 Mechanical Behavior of Plastics

3.0 The Morphology of Hydrated Cements

Personnel: R. B. Williamson and F. Moavenzadeh; K. E. Fusch,
E. Tazawa, D. J. MacFayden, A. J. Mancera, J. N. Sultan and
T. W. Bremner

Sponsorship: The Dow Chemical Company, DSR 70243

The hydration of portland cement is a solidification process that shares many characteristics with the solidification of other materials such as metals or polymers. One objective of this research is to observe the microstructure of portland cement and to determine the morphology of the hydrated components. Another objective is to determine the relationship between structure and properties and, finally, to be able to control properties by controlling the microstructure.

Related Academic Subjects

- 1.41 Strength of Structural Materials
- 1.44 Cementitious Materials
- 1.45 Structural Design of Pavements
- 1.46 Portland Cement Concrete

Theses:

- A. J. Mancera, "The Microstructure and Mechanical Properties of the Portland Cement-Slag System," S.M. Thesis, Department of Civil Engineering, February 1968.
 - E. Tazawa, "Influence of Curing Time on Shrinkage and Weight Loss of Hydrating Portland Cement," S.M. Thesis, Department of Civil Engineering, February 1968.
 - A. J. Mancera and R. B. Williamson, "The Microstructure and Mechanical Properties of the Portland Cement-Slag System," Publication R68-32, Civil Engineering, MIT, May 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.
 - R. B. Williamson and F. Moavenzadeh, "Effects of Flycolic Acid and Dow Latex (Saran) on the Strength and Microstructure of Cement Paste," Proceedings, American Institute of Chemical Engineers Materials Conference, Philadelphia, Pa., April 1968.
- 4.0 The Relationship Between Microstructure and Mechanical Properties of Cementitious Materials

Personnel: R. B. Williamson, F. J. McGarry and R. C. Jones; T. W. Bremner, C. B. Dougherty, G. Farra, A. C. Lemer, D. J. MacFadyen, A. J. Mancera, P. Forootan-Rad, E. Tazawa.

Sponsorship: Advanced Research Projects Agency, SD-90, DSR 78898

The objective of this research is to control the process of hydration of portland cement in order to improve the properties of portland cement concrete. The nucleation (and/or multiplication) and growth of the hydration products are being studied using model systems and the electron microscope on actual samples of portland cement. Most of the electron microscopic

techniques used in the past have not had a realistic water:cement ratio, but these studies have utilized new techniques that limit the amount of water necessary to hydrate the sample.

Related Academic Subjects

- 1.40 Introduction to Electron Microscopy
- 1.44 Cementitious Materials
- 1.46 Portland Cement Concrete

Theses:

- C. B. Doughty, "Viscoelastic and Elasto-Plastic Analysis of a Fiber Reinforced Composite Materials," S.M. Thesis, Department of Civil Engineering, June 1968.
- D. J. MacFadyen, "Structural Aspects of Metal-Matrix Composites," S.M. Thesis, Department of Civil Engineering, February 1968.
- A. J. Mancera, "The Microstructure and Mechanical Properties of the Portland Cement-Slag System," S.M. Thesis, Department of Civil Engineering, February 1968.
- E. Tazawa, "Influence of Curing Time on Shrinkage and Weight Loss of Hydrating Portland Cement," S.M. Thesis, Department of Civil Engineering, February 1968.

Publications:

- C. B. Doughty, "Viscoelastic and Elasto-Plastic Analysis of a Fiber Reinforced Composite Material," Publication R68-89, Civil Engineering, MIT, December 1968.
- D. J. MacFadyen and R. C. Jones, "Structural Aspects of Metal-Matrix Composites," Publication R67-64, Civil Engineering, MIT, December 1967.
- A. J. Mancera and R. B. Williamson, "The Microstructure and Mechanical Properties of the Portland Cement-Slag System," Publication R68-32, Civil Engineering, MIT, May 1968.
- E. Tazawa, "Influence of Curing Time on Shrinkage and Weight Loss of Hydrating Portland Cement," Publication R68-90, Civil Engineering, MIT, December 1968.
- R. B. Williamson and R. S. Markiewicz, "Electron Microscope Study of the Hydration of Portland Cement," Publication R68-57, Civil Engineering,

MIT, June 1968.

5.0 Fibrous Glass Reinforced Plastic Composites

Personnel: F. J. McGarry; A. M. Willner, J. N. Sultan, R. C. Laible

Sponsorship: Air Force Systems Engineering Group, Materials Laboratory,
AF 33(615)-2712, DSR 74969; Dow Chemical Company, DSR 70243

5.1 Microcracking in Fibrous Glass Reinforced Plastics

Study of the parameters controlling microcracking under cyclic loading. Methods of crack detection, measurement. Effects of imposed stress level, number of cycles, orientation of reinforcing fibers, spacing of fibers. Loss of elastic and strength properties. Methods to toughen 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.

17322

5.2 Matrix-Fiber Stress Transfer Mechanisms

Study of stress transfer details in glass fiber-resin composite systems. Direct experimental method to evaluate effects of aspect ratio, glass finish treatments, cyclic loading, exposure to water and toughened resins. Analysis of stresses at ends of fibers, as influenced by geometric details of fiber ends.

17323

Related Academic Subjects

- 1.42 Structural Materials
- 1.471 Mechanical Behavior of Plastics
- 1.472 Composite Materials

Theses:

A. M. Willner, "Toughening of an Epoxy Resin by an Elastomeric Second Phase," Ph.D. Thesis, Department of Civil Engineering, MIT, February 1968.

J. N. Sultan, "Crack Propagation Behavior of Toughened Polyesters,"

S.M. Thesis, Department of Civil Engineering, MIT, January 1968.

Publications:

- J. N. Sultan and F. J. McGarry, "Toughening Mechanism in Polyester Resins and Composites," Publication R67-66, Civil Engineering, MIT, December 1967.
- A. M. Willner and F. J. McGarry, "Toughening of an Epoxy Resin by an Elastomeric Second Phase," Publication R68-8, Civil Engineering, MIT, March 1, 1968.
- F. J. McGarry and A. M. Willner, and J. N. Sultan, "Relationships Between Resin Fracture and Composite Properties", Technical Report AFML-TR-67-381, submitted to Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, December 1967.
- F. J. McGarry and M. Fujiwara, "Glass Fiber-Resin Studies", Proceedings of the 23rd Annual Conference, SPI Reinforced Plastics/Composites Division, Washington, D. C., February 1968.
- F. J. McGarry and A. M. Willner, "Microcracking in Fibrous Glass Reinforced Resin Composites," Proceedings of the 23rd Annual Conference, SPI Reinforced Plastics/Composites Division, Washington, D.C., February 1968.
- F. J. McGarry and A. M. Willner, "Toughening of Crosslinked Resin Systems," Proceedings of the 23rd Annual Conference, SPI Reinforced Plastics/Composites Division, Washington, D. C., February 1968.
- F. J. McGarry and J. N. Sultan, "Rubber Modified Crosslinked Polymers," Proceedings of Regional Technical Conference, Palisades Section, Society of Plastics Engineers, New York City, March 21, 1968.
- F. J. McGarry and J. N. Sultan, "Crack Toughened Resin Formulations," Proceedings of the American Chemical Society Epoxy Resin Symposium, San Francisco, Calif., April 1968.
- F. J. McGarry and A. M. Willner, "Crack Toughened Epoxy Resin Formulations," Proceedings of the American Chemical Society Resin Symposium, San Francisco, Calif., April 1968.
- F. J. McGarry and A. S. Carrara, "Matrix and Interface Stresses in a Discontinuous Fiber Composite Model," J. of Composite Materials, April 1968.
- F. J. McGarry, "Crack Propagation in Fiber Reinforced Plastic Composites," Chapter 5, Fundamental Aspects of Fiber Reinforced Plastic Composites, ed. by R. T. Schwartz and H. S. Schwartz, Interscience

Publishers, New York, 1968.

- F. J. McGarry, "Ductility of the Resin Matrix," Proceedings of the 71st Annual Meeting of American Society for Testing and Materials, San Francisco, Calif., June 27, 1968.
- F. J. McGarry and M. Fuhiwara, "Resin Fiber Load Transfer in Reinforced Plastics," Modern Plastics, Vol. 45, No. 11, 143, July 1968.
- F. J. McGarry, "Toughening Crosslinked Glassy Polymers," Proceedings of the International Symposium on Macromolecular Chemistry, International Union of Pure and Applied Chemistry, Toronto, Ontario, September 6, 1968.

6.0 Viscoelastic Characterization and Analysis

6.1 Viscoelastic Characterization of Engineering Materials

Personnel: F. Moavenzadeh; M. H. Gradowczyk, J. E. Soussou, W. A. Kakel, J. A. Alexander

17324

Sponsorship: Ford Foundation, DSR 76393

The objective of this research is to develop constitutive equations for non-linear 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 non-linear 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. A. Alexander, "Effects of Rubber Additives on Properties of Asphaltic Materials," S.M. Thesis, Department of Civil Engineering, MIT, September 1968.

W. W. Kakel, "Fracture in Asphaltic Mixtures," S.M. Thesis, Department of Civil Engineering, MIT, January 1968.

6.2 Viscoelastic Analysis of Moving Load on Multi-Layer Systems

Personnel: F. Moavenzadeh; J. F. Elliott, J. A. Alexander

Sponsorship: U.S. Department of Transportation, Federal Highway Administration, Bureau of Public Roads, DSR 70604

To develop a numerical technique for solutions of stresses and displacements on three-layer viscoelastic systems subjected to slowly moving load on the surface.

Related Academic Subjects

- 1.45 Structural Design of Pavements
- 1.47 Mechanics of Materials
- 1.471 Mechanical Behavior of Plastics
- 1.473 Viscoelasticity

Publications:

- F. Moavenzadeh and J. F. Elliott, "Moving Load on a Viscoelastic Layered System," Publication R68-37, Department of Civil Engineering, MIT, June 1968.
- F. Moavenzadeh and J. E. Ashton, "Stresses and Displacements in Linear Viscoelastic Bodies," Recent Advances in Engineering Science, Vol. III, 1968, Gordon and Breach Science Publishers Ltd., London.
- F. Moavenzadeh and J. E. Ashton, "Linear Viscoelastic Boundary Value Problems", Journal of the Engineering Mechanics Division, ASCE, Vol. 94, No. EM 1, February 1968.
- F. Moavenzadeh and A. B. Dominguez, "Stresses and Displacements in Semi Infinite Media," Proceedings, Third Pan American Conference on Soil Mechanics and Foundation Engineering, Vol. 1, Caracas, Venezuela, July 1967.

6.3 Analysis of Moving Load on Viscoelastic Layered Systems

Personnel: F. Moavenzadeh; J. F. Elliott, J. A. Alexander

Sponsorship: U.S. Department of Transportation, Federal Highway
Administration, Bureau of Public Roads, DSR 71183

The purpose of this study is to investigate the applicability of a method of analysis of stresses and displacements in layered viscoelastic systems to the development of a rational method of pavement design.

Related Academic Subjects

- 1.45 Structural Design of Pavements
- 1.47 Mechanics of Materials
- 1.473 Viscoelasticity

Publication:

F. Moavenzadeh and A. C. Lemer, "An Integrated Approach to Analysis and Design of Pavement Structure," Publication R68-58, Civil Engineering, MIT, July 1968.

7.0 Structural Metals and Metallic Composites

7.1 Structural Metals

Personnel: R. C. Jones; F. V. Lawrence, Jr., W. R. Navin

Sponsorship: Inter-American Program in Civil Engineering; Ford Foundation, DSR 76392

7.1.1 Cyclic Loading Effects

Study of dislocation arrangements in single crystals of bcc metals as a function of stress level and number of cycles. Constant stress amplitude tests in reversed flexure. Transmission electron microscopy on thin foils cut from test specimens by spark machining. Relation of subgrain structure to macroscopic and microscopic observations.

7.1.2 Loading Rate Effects

Study of macroscopic and microscopic effects of rate of loading in single crystals of high purity iron. Load-deformation observation and work-

hardening rate changes as a function of loading rate and crystal orientation. Dislocation arrangements, observed by transmission electron microscopy, related to macroscopic observations.

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:

- F. V. Lawrence, Jr., "Fatigue Induced Dislocation Structures in Iron Single Crystals," Sc.D. Thesis, Department of Civil Engineering, June 1968.

Publications:

- F. V. Lawrence, Jr. and R. C. Jones, "Fatigue Induced Dislocation Structures in Iron Single Crystals," Publication R68-34, Civil Engineering, MIT, June 1968.
- R. C. Jones and F. V. Lawrence, Jr., "Fatigue Induced Dislocation Structures in Alpha-Iron Single Crystals," Materials Technology - An Inter-American Approach, A.S.M.E., pp. 516-529, (1968).

7.2 Metallic Composites

Personnel: R. C. Jones; D. J. MacFadyen, K. E. Fusch, E. F. Olster

Sponsorship: Dow Chemical Company, DSR 70243; Inter-American Program in Civil Engineering; Ford Foundation, DSR 76392

7.2.1 Structural Applications

Study of the directionality of fiber reinforced metal matrix composites to determine the degree to which the material is inherently anisotropic. Implications of such anisotropy on the structural analysis and design process. Study of mechanism for transferring stresses across joints in

structures fabricated from metal matrix composites. Includes both experimental and analytical components.

7.2.2 Fractography of Aluminum-Boron Composites

The basic objective of this study has been to relate the observed behavior of metal matrix composites to the micromechanical behavior of each component, as surveyed at the fracture surface. The principal method of investigation has been scanning electron micrography.

Application of the scanning microscope to the boron filament aluminum alloy composite system has allowed detailed examination of the components and their interaction in situ. The boron filaments are observed to undergo substantial breakup in the compositing and loading sequence. Incomplete bonding at diffusion bond planes in the matrix metal is found to be a major problem in cross-ply composites of aluminum-boron. Debonding of diffusion bond planes, observed at fracture surfaces, has been observed on a large scale in both cross-ply and unidirectionally reinforced composites.

Observing made of fracture surfaces containing large amounts of incomplete bonding or debonding at diffusion bond planes lead to the conclusion that further optimization of fabrication parameters is needed to improve current state-of-the-art aluminum-boron materials.

7.2.3 Cyclic Stress Response of a Stainless Steel Wire Reinforced Aluminum Alloy Composite

The fatigue behavior of a diffusion bonded stainless steel wire reinforced aluminum alloy composite has been studied, employing the push-pull mode of direct loading. The S-N curve shows an endurance limit of 18 kg/mm^2 and shows a high sensitivity to stress in the high stress, low cycle range.

Microhardness measurements comparing as-fabricated and fatigued samples indicate that little fatigue hardening takes place in the matrix metal. Similar hardness numbers have been observed in all fatigued specimens, regardless of the applied stress amplitude.

Differences are found in relative saturation damping observed during cyclic loading, as a function of stress amplitude. These differences are attributed to different degrees of delamination at the fiber-matrix interface in early stages of the fatigue process. This result is confirmed by optical and scanning electron microscope studies. Fracture surface appearance is substantially different than that found in one-time loaded tensile failures.

7.2.4 Deformation and Fracture of a Metal Matrix Composite Model System

A continuous-fiber metal matrix composite model system has been experimentally developed by combining large diameter (1/16") stainless steel fibers, or rods, with a matrix of high purity aluminum. The model system was designed to compare closely with actual composite systems in the following ways: (1) stress-strain behavior, (2) mode of failure, (3) theoretical predictions of strength, and (4) the development of fiber tensile stress through matrix shear stress transfer.

Results showed the model systems exceeded the rule of mixtures strength predictions, thereby indicating that synergistic effects were present. Microhardness test results verified the existence of high levels of matrix shear stress near the fiber ends.

7.2.5 Diffusion Bonded Scarf Joints in a Metal Matrix Composite

Joints, approaching 100% efficiency, have been obtained in a 2024 aluminum alloy reinforced with 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, was developed for this study.

A wide range of joining parameters provided sound joints; however, the ultimate tensile strength of the joined specimen decreased as bonding times increased.

The high strength scarf joint specimens failed with massive debonding along the diffusion bond planes resulting from the 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, and when subjected to flexural tests could undergo massive deformation with no indication of macroscopic failure.

Related Academic Subjects

- 1.42 Structural Materials
- 1.43 Structural Properties of Metals
- 1.472 Composite Materials

Theses:

- D. J. MacFadyen, "Structural Aspects of Metal Matrix Composites,"
S.M. Thesis, Department of Civil Engineering, September 1967.

Publications:

- R. C. Jones, "Deformation of Wire Reinforced Metal Matrix Composites,"
Metal Matrix Composites, A.S.T.M. STP-438, (1968).
R. C. Jones, "Fractography of Metal Matrix Composites," Proceedings,
14th Refractory Composites Working Group Meeting, Air Force
Materials Laboratory, (1968).
D. J. MacFadyen and R. C. Jones, "Structural Aspects of Metal Matrix
Composites," Publication R67-64, Civil Engineering, MIT,
December 1967.
K. E. Fusch and R. C. Jones, "Deformation and Fracture of a Metal Matrix
Composite Model System," Publication R68-35, Civil Engineering,
MIT, June 1968.

8.0 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 system 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

VIII. SURFACE PROPERTIES AND BEHAVIOR OF MATERIALS SURFACE
LABORATORY, DEPARTMENT OF MECHANICAL ENGINEERING

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:

S. Malkin, Research Assistant, Mechanical Engineering
C. Corrow, Research Assistant, Mechanical Engineering
R. McEntire, Research Assistant, Mechanical Engineering
J. Kirk, Research Assistant, Mechanical Engineering

Support Staff:

Angela Theodore, Secretary, Mechanical Engineering

Degrees Granted:

S. Malkin, Sc.D., Mechanical Engineering, February 1968
G. Grohowski, S.M., Mechanical Engineering, June 1968
W. W. Miller, S. B., Mechanical Engineering, August 1968

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: Un-sponsored

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 electro-polished 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.

2.0 Fundamental Bearing and Seal Research

Personnel: E. Rabinowicz, W. D. Syniuta; C. Corrow

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: N. H. Cook, E. Rabinowicz; 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:

S. Malkin, "The Attritious and Fracture Wear of Grinding Wheels",
Doctoral Thesis, Department of Mechanical Engineering,
February, 1968.

G. Grohowski, "Solid Film Lubrication of Thread Cutting Taps", Master of Science Thesis, Department of Mechanical Engineering, June, 1968.

W. W. Miller, "The Correlation Between the Compatibilities of Alloys and the Compatibilities of Their Constituents", Bachelor of Science Degree Thesis, August, 1968.

Publications:

None

IX. 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

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:

S. A. Doret, Research Assistant, Mechanical Engineering

F. W. Eberle, Research Assistant, Mechanical Engineering

H. P. Miller, Graduate Student, Mechanical Engineering

R. J. Weetman, Research Assistant, Mechanical Engineering

L. E. Sprague, Project Technician, Research Laboratory of Electronics

Degrees Granted:

D. L. Fehrs, Ph.D., Department of Mechanical Engineering,
January 1968

D. S. Shupe, Sc.D., Department of Mechanical Engineering, January
1969

S. A. Doret, M.S., Department of Mechanical Engineering, January
1968

F. W. Eberle, M.S., Department of Mechanical Engineering, January
1968

H. P. Miller, M.S., Department of Mechanical Engineering, January 1968

R. J. Weetman, M.S., Department of Mechanical Engineering, January 1968

Sponsorship:

Research Laboratory of Electronics supported in part by the Joint Services Electronics program under Contract DA 28-043-AMC-02536(E); and in part by National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, Grant No. NGR-22-009-091; and in part by Cabot Solar Energy Fund.

Research Report

The general purpose of our research program is to study problems relating to the atomic, molecular, and electronic processes occurring at 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 the (100) face of tungsten and the (110) face of tantalum. 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

Recently we have formulated a quasi-thermodynamic approach to heterogeneous chemical reactions occurring at gas-solid interfaces. This 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. Both steady-state and transient ("flash desorption") reactions have been considered, and we now plan to extend the treatment to other gas-solid systems.

3.0 Catalytic Reactions at Gas-Solid Interfaces

The abovementioned quasi-thermodynamic approach to heterogeneous reactions is also being applied to catalytic reactions, especially those relevant to the control of air pollution. At present we are considering reactions involving NO, CO, CO_2 , N_2 , and O_2 . The results of these computations will be 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 for several different single-crystal catalysts.

4.0 Scattering of Gas Atoms and Molecules from Solid Surfaces

During the past year we have completed the construction and development of a modulated molecular-beam apparatus designed for investigating 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 Ar atoms from Si(111), Ta(110), and W(110), and for the scattering of Ne from W(110). 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. Our current objective is to obtain similar

data for a variety of beam gases, contaminants, and solid surfaces.

5.0 Absorption, Permeation, and Desorption Processes for Gases Dissolved in Metals

Recently we have developed a theoretical analysis of the permeation of gases through solids which includes the possibility of the rate being limited by surface processes (e.g., adsorption and desorption) as well as by diffusion. The results provide a possible explanation for a wide variety of permeation data that cannot be explained by the diffusion process alone. The analysis is now being extended to transient desorption processes in which the temperature of the solid decreases so rapidly that the gas within the solid may not have sufficient time to escape, thereby resulting in supersaturation. We also plan to construct 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 to the process of "activated adsorption".

6.0 Electrode Processes in Electrical Discharges

During the past year we have conducted experimental and analytical studies of the interaction of arcs or sparks with metallic electrodes, especially for those conditions encountered in electrical discharge machining. The principal objective is to determine the mechanism responsible for the erosion of material from the electrode surfaces. By gaining a clearer understanding of the erosion mechanism, we hope to be able to devise methods for increasing the present levels of tool life and cutting speed of electric discharge machining.

Theses:

- D. L. Fehrs, "Contact-Potential Measurements of the Adsorption of Cs, K, and Na on (110) Ta," Ph. D. Thesis, Department of Mechanical Engineering, January 1968.
- D. S. Shupe, "Theoretical Analysis of the Effect of Surface Processes on the Permeation of Gases through Metals," Sc.D. Thesis, Department of Mechanical Engineering, submitted August 1968 (degree to be awarded January 1969).
- S. A. Doret, "An Experimental Investigation of Electrical Discharge Machining Using a Single Pulse Technique," S.M. Thesis, Department of Mechanical Engineering, January 1968.

- F. W. Eberle, "A Modulated Beam Experiment of the Interaction of Iodine with Tungsten," M.S. Thesis, Department of Mechanical Engineering, January 1968.
- H. P. Miller, "Drag and Lift Coefficients and Evaporation Rate of a Solid in a Rarefied Gas," M.S. Thesis, Department of Mechanical Engineering, January 1968.
- R. J. Weetman, "The Characteristics of DC Arcs as Related to Electrical Discharge Machining," M.S. Thesis, Department of Mechanical Engineering, January 1968.

Publications:

- J. L. Coggins and R. E. Stickney, "Adsorption Studies Based on Thermionic Emission Measurements: I. Cesium on Single-Crystal Tungsten," Surface Sci. 11, 355-369 (1968).
- W. Engelmaier and R. E. Stickney, "Adsorption Studies Based on Thermionic Emission Measurements: II. Oxygen on Single-Crystal Tungsten," Surface Sci. 11, 370-394 (1968).
- W. Greaves and R. E. Stickney, "Adsorption Studies Based on Thermionic Emission Measurements: III. Oxygen on Polycrystalline W, Mo, Ta, and Re," Surface Sci. 11, 395-410 (1968).
- R. E. Stickney, "Low-Energy Molecular Scattering as a Tool for Studying Gas-Solid Interaction Potentials: Comparison of Theory and Experiment," to be published in the Proceedings of the 4th International Materials Symposium on "The Structure and Chemistry of Solid Surfaces" (1968).
- J. C. Batty and R. E. Stickney, "Simple Thermodynamic Model of Reactive Scattering of Gas Molecules from Solid Surfaces: the Oxygen-Tungsten Reaction," to be published in Rarefied Gas Dynamics, Proc. 6th Intern. Symp., Cambridge, Mass., 1968 (L. Trilling and H. Wachman, editors; Academic Press, N.Y., 1968).
- D. L. Fehrs, T. J. Lee, and R. E. Stickney, "Measurements of the Work Function and Desorption Energy of Cesium and Potassium on (100) Tungsten," to be published in Report on 1968 Thermionic Energy Conversion Specialist Conference (IEEE).

X. CRYOGENIC ENGINEERING LABORATORY
MECHANICAL ENGINEERING DEPARTMENT

Faculty:

J. L. Smith, Jr., Associate Professor, Mechanical Engineering
E. G. Cravalho, Assistant Professor, Mechanical Engineering

Graduate Students:

P. M. Andersen, Research Assistant, Mechanical Engineering
H. F. Bowman, Research Assistant, Cryogenic Engineering Laboratory
and Nuclear Engineering Department
Erica L. Coburn, Research Assistant, Mechanical Engineering
K. R. Diller, Research Assistant, Mechanical Engineering
C. Ezekwe, Research Assistant, Mechanical Engineering
L. L. Giventer, Research Assistant, Mechanical Engineering
K. Koenig, Research Assistant, Mechanical Engineering
P. A. Rios y Cartaya, Air Reduction Corporation Fellow
R. S. Rosen, Research Assistant, Mechanical Engineering
T. J. Tennison, III, Research Assistant, Mechanical Engineering
P. Thullen, Hertz Foundation Fellow

Support Staff:

R. P. Cavileer, DSR Staff, Mechanical Engineering
K. H. Benner, Project Technician, Mechanical Engineering
R. D. Gertsen, Technician A
J. O'Callaghan, Machinist
W. J. Shea, Mechanic
Rachel P. Levin, Administrative Assistant
Susan P. Oliver, Secretary

Personnel who have left:

J. Gerstmann, Assistant Professor (To American Electric Power
Service Corp.; returned to MIT September 1968)
F. E. Becker, Research Assistant (Now at General Electric Company,
Lynn, Massachusetts)
H. F. Bowman, Research Assistant (Now at Northeastern University,
Boston, Massachusetts)
E. B. Qvale, Research Assistant (Now at Purdue University, Lafayette,

Indiana)

L. L. Giventer, Research Assistant (Now at Westinghouse Electric Corporation, W. Mifflin, Pennsylvania)

Degrees Granted:

H. F. Bowman, Ph. D. , Nuclear Engineering, June 1968
 D. L. Greene, Naval Engineer and S.M. , Mechanical Engineering, June 1968
 R. J. Howson, Naval Engineer and S.M. , Mechanical Engineering, June 1968
 R. L. Steele, Naval Engineer and S.M. , Mechanical Engineering, June 1968
 G. Trotman, Jr. , Naval Engineer and S.M. , Mechanical Engineering, June 1968
 F. E. Becher, S.M. , Mechanical Engineering, July 1968
 L. L. Giventer, S.M. , Mechanical Engineering, September 1968
 J. D. Shane, S.B. , Mechanical Engineering, September 1968

Sponsorship:

Partly self-supporting
 Lincoln Laboratory, AF 19(628)-5167, P. O. No. A-1681, DSR 76140
 Air Reduction Corporation Fellowship, DSR 21607
 Metal Bellows Corporation (grant-in-aid), DSR 70224
 National Science Foundation (Grant No. GK-3686), DSR 70967

Research Report:

The continuing activities in the Laboratory include: investigation of refrigeration cycles of the Stirling type, application of metal-bellows expansion engines and compressors to miniature cryogenic refrigeration systems, the influence of surface material and surface properties of the boiling heat transfer to liquid helium, the engineering problems of refrigeration below 1°K with He³-He⁴ mixtures, the thermal radiation properties of solids at cryogenic temperatures, the propagation of thermal radiation in absorbing media.

The continuing effort on the application of cryogenics to large scale synchronous generators has progressed to the point that the first laboratory model is operating. The model has a rotating superconducting field winding contained within a 5-inch dewar vessel which rotates at 3600 RPM. A room temperature stator is being designed to take advantage of the high magnetic

field produced by the superconducting winding.

New projects have been initiated on the freezing and thawing of biological cells, and the transient boiling heat transfer to liquid helium for application to the thermal stabilization of superconductors.

The facilities and services of the Cryogenic Engineering Laboratory have continued to be available to and widely utilized by the Institute Community. Approximately 86,000 liters of liquid helium were supplied in the last year.

Theses:

- H. F. Bowman, "Influence on Nuclear Radiation on Pool-Boiling Heat Transfer to Liquid Helium", Ph.D. Thesis, Department of Nuclear Engineering, June 1968.
- D. L. Greene, "Design of a Superconducting Field Magnet for a Synchronous Generator", S.M. Thesis, Department of Mechanical Engineering, May 1968.
- R. J. Howson, "Thermally Sustained Pressure Oscillations in Liquid Helium Apparatus", Naval Engineer and S.M. Thesis, Department of Mechanical Engineering, May 1968.
- R. L. Steele, "The Thermodynamic Properties of Nitrogen-Oxygen Mixtures", Naval Engineer and S.M. Thesis, Department of Mechanical Engineering, May 1968.
- G. Trotman, Jr., "The Pulse Jet - A Propulsive Device for Deep Ocean Vehicles", Naval Engineer and S.M. Thesis, Department of Mechanical Engineering, May 1968.
- F. E. Becker, "A Study of Forced Convection Heat Transfer to Super-critical Helium", S.M. Thesis, Department of Mechanical Engineering, July 1968.
- L. L. Giventer, "Transient Pool-Boiling of Liquid Nitrogen due to a Square-Wave Heat Flux", S.M. Thesis, Department of Mechanical Engineering, September 1968.
- J. D. Shane, "A Study of the Freezing Processes in Biological Cells", S.B. Thesis, Department of Mechanical Engineering, September 1968.

Publications:

- J. W. Colangelo, E. E. Fitzpatrick, S.N. Rea and J. L. Smith, Jr., "An Analysis of the Performance of the Pulse Tube Refrigerator", *Advances in Cryogenic Engineering*, 13, 494-504 (1968).

- P. A. Rios and J. L. Smith, Jr., "The Effect of Variable Specific Heat of the Matrix on the Performance of Thermal Regenerators", *Advances in Cryogenic Engineering*, 13, 566-573 (1968).
- P. Thullen and J. L. Smith, Jr., "Model for Thermally Sustained Pressure Oscillations Associated with Liquid Helium", *Advances in Cryogenic Engineering*, 13, 215-222 (1968).
- E. B. Qvale and J. L. Smith, Jr., "A Mathematical Model for Steady Operation of Stirling-Type Engines", *Transactions of ASME, J. of Engineering for Power*, pp. 45-50, January 1968.
- P. A. Rios, E. B. Qvale and J. L. Smith, Jr., "An Analysis of the Stirling-Cycle Refrigerator", presented at the 1968 Cryogenic Engineering Conference (to be published in *Advances in Cryogenic Engineering*, Vol. 14 ((Paper J-1))).
- C. L. Tien and E. G. Cravalho, "Thermal Radiation of Solids at Cryogenic Temperatures", *Advances in Cryogenic Heat Transfer, Chemical Engineering Progress Symposium Series*, Vol. 64, 87, 56-67 (1968).
- E. G. Cravalho, G. A. Domoto, and C. L. Tien, "Measurements of Thermal Radiation of Solids at Liquid-Helium Temperatures", preprint, Paper No. 68-774, presented at AIAA 3rd Thermophysics Conference, June 24-26, Los Angeles, California.
- E. G. Cravalho and C. L. Tien, "A Study of Thick Film Solutions for Radiative Transfer between Two Dielectrics", preprint, Paper No. 68-HT-34, presented at the 11th Annual Heat Transfer Conference, ASME-AIChE, August 11-14, 1968, Philadelphia, Pennsylvania.

XI. CHEMICAL ENGINEERING OF MATERIALS

1.0 Properties of Complex Coacervates of Polyelectrolytes

Faculty:

A. S. Hoffman, Associate Professor, Chemical Engineering

Graduate Student:

D. Wu, A. D. Little Fellow, Chemical Engineering

Sponsorship:

None at present

Research Report

The mechanical properties of complex coacervates of polyanions and polycations are being investigated. The major material variable is the charge density on the individual polyelectrolyte backbones. This is controlled by the ratio of charged to non-charged monomers used to prepare the polyanions or polycations by copolymerization. Swelling and salt sorption data of the coacervates are being obtained in order to extend the theory of complex coacervation to coacervates of varying, controlled charge density. These data enable modelling of the microstructure and thus better interpretation and understanding of the mechanical properties.

2.0 Reverse Osmosis Desalination Membranes

17326

Faculty:

A. S. Hoffman, Associate Professor, Chemical Engineering
M. Modell, Assistant Professor, Chemical Engineering

Graduate Students:

T. A. Jadwin, Research Assistant, Chemical Engineering
A. Azizoglu, Research Assistant, Chemical Engineering
R. Leonard, Research Assistant, Chemical Engineering
P. Pan, Research Assistant, Chemical Engineering
M. Sze, Research Assistant, Chemical Engineering

Sponsorship:

Office of Saline Water, U. S. Dept. of Interior, Grant No. 14-01-0001 - 1256, DSR 70641

Research Report

New Membranes for desalination by reverse osmosis are being prepared by polymerization techniques from a variety of different monomer mixtures. Two "families" of membranes have been developed: (1) hydroxy ethyl methacrylate + methacrylic acid + trimethylol propane trimethacrylate and (2) N-methylol acrylamide + acrylic acid + ethylacrylate (or butyl methacrylate) + trimethylol propane trimethacrylate.

The membranes are first characterized as to salt and water contents in salt solution. There the direct osmosis of salt is measured and finally reverse osmosis under high pressure is studied as a function of salt content (osmotic pressure) and hydrostatic pressure.

Recent membranes developed are as good as the best membranes currently available (cellulose acetate) and attempts are being made to surface polymerize these monomer mixtures on porous supports. New membrane compositions are also being studied.

3.0 Catalysis3.1 Interphase Electronic Interactions in Polyphase Solid Catalysts

Faculty:

R. F. Baddour, Professor, Chemical Engineering
M. C. Deibert, Assistant Professor, Chemical Engineering

Graduate Student:

R. W. Kline, Graduate Student, Chemical Engineering

Sponsorship:

National Science Foundation GK-1699X, DSR 70558

Research Report

Catalysts are prepared with measured surface areas of nickel deposited on germanium cleaned at high vacuum. Investigations are being carried out to determine the activity of these catalysts for ethylene hydrogenation as the electronic properties of the germanium and the thickness of the nickel surface layer are varied.

3.2 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

Support Staff:

S. R. Mitchell, Project Technician, Chemical Engineering

Sponsorship:

National Science Foundation GK-1699X, DSR 70558

Research Report

The objective of this program is to develop a general method of determining the mechanisms of gas-phase, metal-catalyzed reactions. A method has been proposed, which consists of measuring simultaneously the overall reaction rate and the concentrations of surface intermediates as functions of temperature and reactant pressures. Infrared spectroscopy is used to measure surface concentrations. Postulated mechanisms can then be tested directly by comparing experimental and theoretical forms of the rate, expressed in terms of surface concentrations.

In an experimental program initiated in 1963, simultaneous infrared and kinetic measurements were made for CO oxidation on silica-supported palladium catalysts. For the CO-Pd system, two types of surface species were identified by infrared spectroscopy. Palladium-oxygen absorption bands were not observed because the background absorption of the silica support is intense in the region where Pd-O₂ bands are believed to occur. The results indicated clearly the inadequacy of the conventional kinetic approach and the value of simultaneous 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. The investigations now in progress are aimed at developing methods for obtaining

the additional data.

A program is in progress for obtaining absolute values of surface concentrations by measuring the relative extinction coefficients of absorbed species. The method essentially involves relating the increase in total amount of gas adsorbed during sequential dosing of a catalyst with adsorbate to the relative increase in integral absorbance of the infrared bands. When the extinction coefficients have been determined, simultaneous measurements of kinetics and spectra will be made over wide ranges of surface coverage. In this investigation, the catalysts are silica-supported metals of the type previously used for infrared transmission spectroscopy of adsorbed species.

A second set of experiments is in progress to develop general techniques for observing infrared absorption bands of all surface species. The conventional infrared method involves transmission spectroscopy in which small particles of metal (50 Å) are supported on finely divided silica or alumina (100 Å). Large regions of the infrared are obscured by the intense adsorption of these supports. Thus, palladium-oxygen bonds have not been observed because they are believed to occur in the region of the silica continuum. In an effort to surmount the limitations of conventional transmission spectroscopy, 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 1% of a monolayer in the range of 250 to 2500 cm^{-1} . To date, the apparatus has been assembled and preliminary experiments are in progress. Tests were made to determine the sensitivity of the interferometer and the reflectivity of the metal foils. The first tests with carbon monoxide adsorbed on palladium foils have been made recently and the results are very encouraging; we believe that we are observing absorption bands which correspond to known CO surface species. 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.

A third study was recently initiated with the objective of measuring and correlating the rates of adsorption and desorption of gases on transition metals. There have been very few attempts made to correlate quantitatively rates of adsorption and desorption. Within recent years, it has become evident that these processes are not simple; for a given gas and a given metal, many surface species are known to coexist. The techniques we are

developing to study mechanisms of catalyzed reactions are directly applicable to the study of adsorption and desorption processes. Thus, by observing overall rate of adsorption and infrared spectrum of the surface, it should be possible to measure the adsorption rates of each surface species. Such experiments are planned for a given gas on a series of metals. In this manner, it is hoped that the rate of adsorption of each type of surface species can be observed on different metals. An attempt will be made to correlate these rates with electronic and geometric properties of the metals.

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).

4.0 Biomaterials

4.1 Non-Thrombogenic Polymers, and Aerosol Surfactants for Pulmonary Therapy

17327

Faculty:

E. W. Merrill, Professor, Chemical Engineering
K. A. Smith, Associate Professor, Chemical Engineering
E. R. Gilliland, Professor, Chemical Engineering

Research Staff:

P. S. Wong, Chemical Engineering
E. W. Salzman, Beth Israel Hospital
W. Gerald Austen, Massachusetts General Hospital
J. Folkman, Children's Medical Center
H. Kazemi, Massachusetts General Hospital
D. Shannon, Massachusetts General Hospital

Graduate Students:

D. A. Grindstaff, Research Assistant, Chemical Engineering
G. A. Mellinger, Research Assistant, Chemical Engineering
S. M. Nemser, Research Assistant, Chemical Engineering
A. D. Skibo, Research Assistant, Chemical Engineering

Degrees Granted:

- G. A. Mellinger, S.M., Chemical Engineering, June 1968
- S. M. Nemser, S.M., Chemical Engineering, June 1968
- A. D. Skibo, S.M., Chemical Engineering, September 1968

Sponsorship:

- U. S. Public Health Service, 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 methacrylates.

Applications include dialysis and oxygenation membranes, and implantable prostheses.

Aerosols based on lecithin, prepared in the Department of Chemical Engineering, are being studied clinically in the Pulmonary Unit of Massachusetts General Hospital. These aerosols have low surface tension, varying with surface area like the lung surfactant, and enhanced stability against evaporation.

Theses:

- G. A. Mellinger, "Ionic Bonding of Heparin to Amines," S.M. Thesis, Department of Chemical Engineering, June 1968.
- S. M. Nemser, "Non-Thrombogenic Silicone Rubbers," S. M. Thesis, Department of Chemical Engineering, June 1968.
- A. D. Skibo, "Synthesis of Polyethylterephthalamide," S.M. Thesis, Department of Chemical Engineering, September 1968.

Publications:

- D. C. Shannon, M.D., H. Kazemi, M. D., E. W. Merrill, K. A. Smith, P. S. Wong, "Lung Surface Activity: Restoration with a Lecithin Fog," Proceedings, 2nd NIAMD Contractors Conference -- Artificial Kidney Program, Silver Spring, Maryland, January 1969.

4.2 Structure and Properties of Elastin

Faculty:

A. S. Hoffman, Associate Professor, Chemical Engineering

Graduate Students:

D. Mukherjee, Research Assistant, Chemical Engineering

K. Misnacioglu, Research Assistant, Chemical Engineering

Sponsorship:

The Medical Foundation

Research Report

The swelling behavior and elastic creep behavior of purified elastin from cow ligament are being studied in order to help elucidate the molecular organization of the elastin in ligament.

5.0 Cryogenic Chemistry

Faculty:

R. C. Reid, Professor, Chemical Engineering

M. W. P. Strandberg, Professor, Physics

Graduate Student:

G. Rappe, Research Assistant, Chemical Engineering

Sponsorship:

National Science Foundation, GK-1021, DSR 76384

Research Report

Reactions of atomic hydrogen with solid isobutylene at 77 degrees K have been studied using an electron spin resonance spectrometer to monitor the gas phase hydrogen atom concentration during the course of the reaction. Thin films (1.0 - 10.0 micron) of olefin were condensed from the gas phase on the walls of an all-quartz spherical resonance cavity. Atomic hydrogen was generated in the gas phase by a microwave discharge. Reactions were conducted at constant hydrogen pressure to reduce fluctuations in the concentration of hydrogen atoms. Experimental rates of reaction were determined by monitoring the loss of hydrogen from an upstream vessel.

The object of this study is to elucidate the mechanism of this gas-solid

system in which simultaneous diffusion and chemical reaction occur. Experimental variables such as film thickness, olefin and hydrogen atom concentration are being 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. Preliminary experiments indicate agreement between experimental rates of reaction and reaction rates predicted by a simultaneous "bulk" and "surface" model.

6.0 Diffusion and Reaction in Porous Materials

Faculty:

C. N. Satterfield, Professor, Chemical Engineering

Graduate Students:

J. R. Katzer, Graduate Student, Chemical Engineering

C. Cheng, Graduate Student, Chemical Engineering

Personnel who have left:

W. G. Margetts (Now at Norton Company, Worcester, Mass.)

Sponsorship:

National Aeronautics and Space Administration (Center for Space Research NsG-496 (part), DSR 76183

National Science Foundation, GK-1707, DSR 70554

Research Report:

The recently completed Sc. D. thesis of Margetts focussed on the sorption capacity and diffusion characteristics of single crystals of the molecular sieve Na-mordenite. Studies were made at temperatures of 25 to 110°C, and partial pressures of 1 -30 torr. Compounds studied included methane, n-butane, iso-butane 1-butene, perfluorobutane, water, SF₆, krypton and a few cyclic hydrocarbons. These choices were made on the basis of special features of molecular size, shape, or intermolecular forces.

Data were obtained in a constant volume system in which the decrease in pressure was monitored as a function of time. The apparatus consisted of a pressure sensing unit which enabled pressure measurements to be

made only a few seconds after introduction of the sorbate gas. Additional studies were also made in a constant pressure apparatus in which the sorption process was studied.

A number of mathematical models were considered in order to analyze the data. These models were concerned with both undimensional and spherical geometries and covered constant and variable surface concentrations of sorbate as boundary conditions.

Diffusion in zeolites is a complicated process and cannot be precisely represented by a Fick's law type relationship. However, of the mathematical models considered, the data are best fitted by a model representing diffusion into a spherical particle from a gas phase of constant volume. At 25°C a Fick's law diffusivity of methane decreased with increasing pressure but the opposite effect was observed with butanes and butene. Reasons for this behavior are advanced. Presorption of water vapor increased the diffusivity of hydrocarbon molecules subsequently sorbed. The heats of sorption for methane, isobutane and perfluorobutane are approximately 7.9, 8.5 and 10.0 kcal/mole, respectively, at low fraction of equilibrium sorption capacity.

The recent advent of molecular sieve catalysts is having major impact on the processing of hydrocarbons, particularly in petroleum refining. The reasons for their unusual reaction characteristics are far from clear but it is evident that the diffusional characteristics of product and reactant molecules in the extremely tiny pores in the catalysts can profoundly affect the course of the reaction. Mr. James R. Katzer is studying the alkylation of benzene with propylene to form cumene as a model reaction system to characterize some of the phenomena that occur in zeolite catalysis. Work thus far has focussed on the diffusion characteristics of benzene and cumene in the liquid phase in two zeolites of commercial importance: hydrogen mordenite and Type Y zeolite, both studied as powders comprising individual crystals. Diffusion rates of benzene and cumene in hydrogen mordenite have been found to be very slow and counterdiffusion of the two species does not occur within the mordenite pores. Since hydrogen mordenite is known to be an active catalyst for the alkylation of benzene to cumene, this leads to the important conclusion that, at least for molecules of this size, reaction probably all occurs on catalyst sites outside the pores. Studies of the diffusion of cumene in hydrogen mordenite show that the diffusion coefficient decreases substantially with an increase in the length of time that the cumene had been in contact with the zeolite before the diffusion run was carried out. Studies by electron spin resonance show that radical ions are formed when cumene is in contact with hydrogen mordenite and periods of many hours or

days at room temperature are required for the maximum intensity signal to be reached. A gradual blocking of the pores may be occurring by chemisorption or by the formation of larger molecules from the cumene. Studies with Type Y sodium zeolite and the same material after being ion-exchanged to form a catalytically active material show a dramatic increase in the diffusion rate with the nature of the cation present. This has considerable implications in catalysis since it implies that reports of the effect of the nature of various cations on zeolite activity may represent, at least in part, a physical effect rather than a variation in intrinsic chemical reactivity.

Theses:

- W. G. Margetts, "Diffusion and Sorption Characteristics of the Zeolite Na-Mordenite," Sc.D. Thesis, Department of Chemical Engineering, June 1968.

Publications:

- C. N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," to be published in the near future by the MIT Press. This book contains a detailed analysis of methods of predicting diffusion rates in finely porous materials with particular application to the effects of diffusion on the performance of solid catalysts.

XII. EFFECTS OF RADIATION ON MATERIALS

1.0 Effects of Radiation on Organic Coolants for Nuclear Reactors

Faculty:

E. A. Mason, Professor, Nuclear Engineering

Research Staff:

W. N. Bley, Research Associate, Nuclear Engineering

S. T. Brewer, DSR Staff, Nuclear Engineering

Graduate Students:

M. L. Lee, Research Assistant, Nuclear Engineering

G. Yadigaroglu, Research Assistant, Nuclear Engineering

G. Rigamonti, Research Assistant, Nuclear Engineering

H. Spierling, Research Assistant, Nuclear Engineering

C. K. Anderson, Graduate Student, Nuclear Engineering

Support Staff:

R. Cooney, Northeastern University Cooperative Student

S. Parkhurst, Northeastern University Cooperative Student

E. Pembroke, Northeastern University Cooperative Student

B. Stone, Northeastern University Cooperative Student

A. J. Pierni, Chemical Technician, Nuclear Engineering

J. F. Howard, Chemical Technician, Nuclear Engineering

Susan Kelemen, Secretary, Nuclear Engineering

Constance DeFusco, Secretary, Nuclear Engineering

Degrees Granted:

M. L. Lee, Ph.D., Nuclear Engineering, September 1968

H. Spierling, S.M., Nuclear Engineering, June 1968

C. K. Anderson, S.M., Nuclear Engineering, January 1968

Sponsorship:

Atomic Energy Commission, Savannah River Operations Office,

Contract No. AT(38-1)-334, DSR 79819

Research Report:

Irradiations of the terphenyl mixtures, Santowax OM and WR, were made in the MIT In-pile Loop Facility at temperatures ranging from 300°C (572°F) to 427°C (800°F). These potential coolants for nuclear reactors were irradiated while flowing through a stainless steel in-pile loop installed in a special fuel element in central position (Fuel Position 1) of the MITR. Steady-state operating conditions were maintained by continually removing coolant samples from the loop and feeding processed coolant to the loop. The coolant samples were processed using a High Boiler (HB) distillation procedure to remove HB. The distilled terphenyls and Low and Intermediate Boilers (LIB) were returned to the loop along with fresh makeup.

The dose rates to the terphenyl coolant due to fast neutrons and gamma-rays were measured using adiabatic calorimeters. Resonance and threshold foils were used as a check on the calorimetric measurements of the fast neutron fraction of the total dose rate. This fraction was 0.36 for the Santowax OM irradiations and 0.38 for the Santowax WR irradiations. The MITR was operated at 5 MW thermal power except for three of the Santowax OM irradiations, when the power was 2 MW. The average dose rate to the total coolant was 0.057 and 0.067 watts/gram at 5 MW (0.02 watts/gram at 2 MW) and the in-core dose rate to the coolant was 1.2 and 1.3 watts/gram at 5 MW (0.47 watts/gram at 2 MW).

Three steady-state low temperature (300°C) irradiations of Santowax OM were made at different terphenyl concentrations to determine the apparent reaction order for radiolysis and the rate constants for degradation by radiolysis. The results indicated an apparent reaction order of radiolysis of 1.7 ± 0.1 , which is the same value reported by MIT earlier for meta-rich terphenyls. The fast neutron effect ratio, G_N/G_γ , of 3.3 was estimated for the total terphenyl in Santowax OM. Using these values to allow for the effects of coolant composition and fast neutron fraction, the radiolytic rate constants were found to be in good agreement with the results of low temperature irradiations of Santowax OM made at various fast neutron fractions by the other laboratories.

Of the nine high temperature (above 350°C) irradiations, three were made at 2 MW reactor thermal power with Santowax OM, three at 5 MW with Santowax OM, and three at 5 MW with Santowax WR. The results of these high temperature irradiations were correlated using a degradation model which assumes that the rate of total degradation represents the linear sum of radiolysis and radiopyrolysis (i.e., pyrolysis of irradiated coolant). No significant differences were found in the first-order radiopyrolysis rates for

Santowax OM and WR. No significant difference was observed in the rate of radiopyrolysis for Santowax OM due to a change in the dose rate. Combining the recent results with results of earlier irradiations at MIT, the best estimate of the first-order radiopyrolysis rate constants for irradiated Santowax OM and WR is

$$k_{P,omp,1}(T) = \exp(a - \Delta E_p/RT)$$

where

$$a = 34 \pm 7, \Delta E_p = 54 \pm 9 \text{ kcal/mole}$$

Six autoclave pyrolysis experiments were made, three with unirradiated Santowax WR and three with irradiated Santowax WR. Thermal decomposition rates of the unirradiated coolant are significantly lower than those of the irradiated coolant. The latter are not significantly different from those determined during steady-state in-pile irradiation.

Theses:

- M. L. Lee, "Effect of Reactor Irradiation on Santowax OM and WR," Ph.D. Thesis, Department of Nuclear Engineering, September 1968.
- C. K. Anderson, "A Conceptual Design of a Catalytic Hydrocracker to Reclaim Degraded Organic Coolant from the MIT Reactor," S.M. Thesis, Department of Nuclear Engineering, January 1968.
- H. Spierling, "Heat Transfer Characteristics of Santowax WR in Forced Convection and Pool Boiling," S.M. Thesis, Department of Nuclear Engineering, June 1968.

Publications:

- E. A. Mason, M. L. Lee, W. N. Bley, "Comparison of Degradation Rates of Santowax OM and WR," Trans. Am. Nuc. Soc. 10, 480 (November 1968).

17324 2.0 Radiation Acceleration of Viscoelastic Processes in Polymers

Faculty:

E. R. Gilliland, Professor, Chemical Engineering
A. S. Hoffman, Associate Professor, Chemical Engineering

Graduate Students:

R. Mayer, Research Assistant, Chemical Engineering
K. Nisancioglu, Undergraduate Student, Chemical Engineering

Sponsorship:

Atomic Energy Commission, purchase order from Lawrence Radiation
Laboratories, Livermore, California, under Contract W-7405-ENG-
48, DSR 70049, 74678, 70626

Research Report:

The temporary acceleration of creep during high intensity irradiation of polycarbonate is being investigated and it is concluded that the effect is due to the act of generation and temporary accumulation of gases between the polymer chains.

Theses:

K. Nisancioglu, "Effect of Initial Density and Annealing Conditions on Accelerated Creep in Polycarbonate," S. B. Thesis, Department of Chemical Engineering, June 1968.

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 field up to 255 kilogauss. Superconducting magnets with fields to 80 kG and a large variety of pulsed magnets with fields to 750 kG are also in use. The development of magnets to provide even higher fields and to meet special experimental requirements is continuing.

The laboratory's research program is primarily a study of the magnetic, electrical, optical and acoustic properties of matter with the aim of increasing understanding of the electronic band structure, the lattice vibration spectrum, phonon-electron interactions and magnetic interactions in solids. A strong magnetic field represents a perturbing environment which alters the effect of materials on the transmission and reflectance of electromagnetic and acoustic radiation. Experimental techniques now in use include single photon, multiphoton and non-linear magneto-optical reflection and absorption, de Haas-van Alphen effect, magnetic resonance, magnetoresistance, Mossbauer effect and acoustic absorption. The use of intense laser light sources and ultra low temperatures with high magnetic fields provides many new experimental opportunities. Theoretical studies of band structure, magnetism, superconductivity and other topics are carried on in close conjunction with the experimental program. The high field facilities are made available to research groups from other MIT departments and from institutions throughout the world.

Sponsorship

Francis Bitter National Magnet Laboratory
Supported by the Air Force Office of Scientific Research
Contract F44620-67-C-0047

FRANCIS BITTER NATIONAL MAGNET LABORATORY

Personnel:

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

Dr. R. W. Arndt*

Professor A. E. Bergles

R. Bierig**

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

M. H. Weiler

R. J. Weggel

Professor J. Zak**

Visiting Scientists:

Dr. N. A. Blum (NASA - Electronics Research Center)

Dr. J. Chappert (Centre d'Etudes Nucleaires de Grenoble)**

Dr. J. Dimmock (Lincoln Laboratory)

Dr. R. Doclo (Belgian-American Educational Foundation)**

Professor M. Dresselhaus (Professor of Electrical Engineering, MIT)

Dr. F. Dupre (University of Rome)**

S. Fischler (NASA - Electronics Research Center)

I. De Grave (University of Louvain)
Professor R. P. Guertin (Tufts University)
Professor A. Javan (MIT Physics Department)
Dr. J. Korving (University of Leiden)**
Dr. L. Meyers (Boston University)
Dr. R. O'Brien (Weston College)
Professor F. Pollak (Brown University)
Dr. M. Ricci (University of Rome)**
Dr. K. Tachikawa (National Research Institute for Metals, Tokyo)**
Dr. J. Traff (Technical University of Denmark)**
Professor G. Zimmerman (Boston University)

Graduate Students:

D. Abeshouse, Graduate Student, Physics (Boston University)
T. Bernstein, Graduate Assistant, Physics (MIT)
A. Brecher, Graduate Student, 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 Student, Physics (Tufts)
M. Maltz, Graduate Assistant, E. E. (MIT)**
G. Peabody, Graduate Student, Physics (Harvard)
M. Reine, Graduate Student, Physics (MIT)
U. Smith, Graduate Student, Physics (MIT)
R. Stimets, Graduate Assistant, Physics (MIT)

*Leave of Absence

**Terminated during 1968

Degrees Granted:

Martin Sidney Maltz, Ph.D., Electrical Engineering, June 1968, "A
Magnetoreflexion Study of Arsenic and Bismuth".
Peter Warren Staecker, S.M., Electrical Engineering, September 1968,
"High Resolution Magneto-Reflection of Indium Antimonide".
Aviva Brecher, S.B. and S.M., Physics, September 1968, "Cyclotron
Resonance Quantum Effects in p-type Semiconductors".

Larry D. Flesner, S.B., Physics, June 1968, "Magnetic Field Dependence of the Thermoelectric Power of n-InSb".

Richard Q. Fox, S.B., Physics, June 1968, "The Use of Superconducting Cylindrical Tubes to Maintain High Intensity Shaped Inhomogeneous Magnetic Fields".

FRANCIS BITTER NATIONAL MAGNET LABORATORY
RESEARCH REPORTS

1.0 High Field Magnet Development

Personnel: A. Bergles, R. Hale, Y. Iwasa, H. Kolm, M. Leupold,
B. Montgomery, C. Weggel, R. Weggel, N. Pierce (MIT Consultant)

Sponsorship: Air Force Office of Scientific Research F44620-67-C-0047

Research Report:

The first hybrid magnet is nearing completion and final test. The system will combine a 165 kG, 5 MW water-cooled copper insert with a 35-cm room temperature bore 60 kG superconducting magnet to produce 225 kG. Fifteen thousand feet of 1-cm by 2-mm NiTi copper composite material have been used in the superconducting section, the conductor consisting of 66 strands of superconductor co-drawn in a copper matrix. Sufficient cooling surface is provided to assure full stability against field collapse, even under the conditions of the 10% over-current induced by any sudden field collapse of the water-cooled inner section. The cryostat has been designed to support the very large magnetic interaction forces by means of stainless-steel cable supports similar to the spokes of a bicycle wheel assembly. Helium losses are expected to be 6 liters/hour when running at full current. Helium will be removed from the cryostat between magnet runs, and the coil held at 20°K by a small regenerative refrigerator.

The Laboratory's 25 water-cooled magnets, generating fields from 100 to 225 kG, have been operated in various combinations throughout the year on a three shift per day basis. Reliability has been increased to the point where magnets routinely absorb in excess of a million kilowatt hours before requiring maintenance. Reduction of stress concentrations in the 150 kG and 225 kG magnets as well as the introduction of beryllium-copper conductors at the highest field level have been particularly effective.

Considerable progress has been made toward understanding the behavior of understabilized composite superconductors in magnets. Study of the recovery of such conductors following induced flux jumps has allowed development of a computer model which can accurately predict magnet performance as a function of the amount of stabilizing material and the

cooling conditions. A standard test has been developed to predict magnet performance from tests on short pieces of material, and has been used to evaluate materials for a number of other laboratories. Inorganic insulators and effective interlayer materials have been developed. A number of basic measurements on transient heat transfer, heat capacity, and thermal conductivity have been made in conjunction with the investigation of composite material behavior. Investigation of V_3Ga tapes and twisted composite materials have also been undertaken and a new 75 kG homogeneous 35-mm bore superconducting magnet has been built.

Publications:

- MS 450 Y. Iwasa and J. E. C. Williams, "Macrovortex Structure in Hard Superconductors," J. Appl. Phys. 39, 2547-2560 (May 1968).
- MS 451 J. R. Hale and J. E. C. Williams, "The Transient Stabilization of Nb_3Sn -Composite Ribbon Magnets," J. Appl. Phys. 39, 2634-2638 (May 1968).
- JP 292 D. Bruce Montgomery and Y. Iwasa, "Concerning the Reduction of Liquid Helium Consumption in Superconducting Magnet Operation," Cryogenics 8, 247 (August 1968).
- JP 293 D. Bruce Montgomery and B. B. Schwartz, "Hybrid Magnet Program," Phys. Today 21, 65-67 (June 1968).
- TR 12 M. P. Fiori and A. Bergles, "Model of Critical Heat Flux in Subcooled Flow Boiling," Rep. 70281-56 (September 1968).
- JP 283 D. B. Montgomery and L. Rinderer, "A High Current Density 9 Kilojoule Superconducting Magnet without Degradation," Cryogenics 8, 221-224 (August 1968).

2.0 Magnetic Proof-loading of Aircraft Structures

Personnel: H. H. Kolm, D. B. Montgomery

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Ever since the development of metal aircraft, airframe structures and skin sections have been secured by rivets. Rivets produce stress concentrations which make it impossible to develop the full potential strength of skin-stressed structures, and riveted structures offer very little inherent

damping to reduce fluttering and consequent fatigue. The use of modern epoxy bonding methods would alleviate both of these shortcomings and also permit the use of entirely new structural-members such as bonded integral honeycomb-skin panels of great inherent stiffness and high damping. The use of bonded structures in the aircraft industry has been precluded thus far by the lack of a non-destructive testing method applicable to production as well as in-service inspection procedures. What is needed, basically, is a non-destructive method of applying traction forces of several thousand psi to proof-load an aircraft skin surface. The Boeing Company has succeeded in applying such forces by passing currents of several thousand amperes per centimeter through test panels subjected simultaneously to a transverse magnetic field of high intensity. Unfortunately, this technique is destructive, and would not lend itself to use of large structures. The Boeing Company approached us in September with a request for assistance.

As early as 1960, we had provided similar assistance to the Corvair Corporation in their development of magnetic forming methods now generally used to secure control cables to turnbuckles and torque transmission tubes to drive-shifts (the "Magnaform Process"). In this connection we had conceived of a novel technique capable of exerting traction rather than repulsion forces, which seems well suited to Boeing's requirements. The method involves the use of two simultaneous pulsed magnetic fields: a slow pulse which permits a magnetic field to penetrate into the aluminum, and a fast pulse which generates an eddy current in the surface of the aluminum, the two pulses being suitably timed and oriented with respect to each other.

Under Boeing sponsorship, an initial prototype testing device is now nearing completion. The penetrating field will be provided by one of our continuous magnets, and the fast pulse is generated by a specially developed double spark gap capable of crowbarring a highly underdamped oscillatory discharge after the first half-cycle of six microsecond duration. Initial calibration runs are now in progress.

3.0 Magnetic Ore Separation

Personnel: H. H. Kolm, D. B. Montgomery

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The force which can be applied magnetically to a particle is proportion-

al to particle size, induced magnetization, and applied magnetic field gradient. The art of magnetic ore separation is in a very rudimentary state and has been applied successfully only to highly ferromagnetic particles of relatively large size. The availability of more intense magnetic fields and higher field gradients from superconducting and cryogenic magnets has made it economically possible to apply magnetic separation to materials not previously amenable to the technique, notably paramagnetic materials (which are not adequately magnetized in conventional magnets) and weakly magnetic colloidal materials (which are too small for the gradients achievable in existing separators). In cooperation with a Georgia clay mining company, we have succeeded in developing a magnetic separator capable of removing dark colored impurities containing trace quantities of iron from kaolin (a white clay). The new separator utilizes magnetically saturated stainless steel wool to achieve a large volume of high field gradient. Following successful pilot plant tests, a unit of industrial capacity is now under construction. The purified kaolin is used primarily in the coated paper industry.

Tests are also being made in an effort to apply magnetic separation to other materials. In collaboration with the Climax Molybdenum Company, we are attempting to separate non-sulfide molybdenum and tungsten from what now represents tailings from the molybdenum sulfide floatation, not economically recoverable by chemical methods. Initial experiments indicate that the separation may be feasible, but will require a different approach from the one used in clay separation. Another collaboration has just been started with the Kennecott Copper Company in an effort to find means for magnetically classifying some of the numerous minerals found in ocean bottom sediment. The highly dispersed state in which ocean bottom minerals are found suggests that magnetic separation may prove to be the key to recovering this vast resource of minerals. It is too early to evaluate the likelihood of success.

4.0 Medical Magnet Project

Personnel: D. B. Montgomery, R. Weggel, N. T. Pierce (MIT Consultant)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

For the past two years the Magnet Research and Development Group

has collaborated with the Neurosurgery Service at Massachusetts General Hospital on a project to guide permanent magnet tipped catheters through the blood vessels in the neck and head by means of an external magnet. A relatively large iron magnet orientable in 3 axes and driven by a 5 kilowatt supply was designed and built. Special auxiliary devices such as a no-leakage frictionless catheter introducer and special inflatable catheter tips have been developed in this Laboratory for use with the system. Experiments performed on animals have confirmed the usefulness of the concept in catheterizing areas unreachable without the magnetic guidance.

Publications:

JP 253 S. B. Yodh, N. T. Pierce, R. J. Weggel and D. B. Montgomery,
"A New Magnet System for 'Intravascular Navigation'," J. Medical
and Biological Engineering 6, 143-147 (May 1968).

5.0 Limiting Effects in High Field Superconductors

Personnel: S. Foner, E. J. McNiff, R. Meservey, B. B. Schwartz;
K. Tachikawa (National Research Institute for Metals, Tokyo)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Magnetic moment, rf loss, and transverse magnetoresistance measurements on high field superconductors are being continued to investigate various limiting factors in high field superconductors. The H_{c2} versus T measurements are being extended (down to 0.35°K in order to examine systematic deviations from predictions. Selected large α materials (such as the TiV alloys) and thin films are being studied for possible first order magnetic phase transitions at these lower temperatures. Several practical wires (such as V_3Ga) and thin films are also being examined with long pulsed fields when the critical field exceeds available dc fields.

Publications:

MS 336 E. Maxwell, B. B. Schwartz and H. Wiggall, "Flux Hole Motion and the Peak Effect in Superconductivity," Proc. LT 10, Vol. II-B (Moscow, 1967) pp. 52-57.

MS 449 E. Maxwell, B. B. Schwartz, H. Wizgall and K. Hechler, "Peak Effect Studies on Niobium Nitride," J. Appl. Phys. 39, 2568-2571 (May 1968).

6.0 Exchange Enhancement in Metals and Alloys

Personnel: S. Foner, E. J. McNiff, R. Doclo (University of Ghent),
I. De Grave (University of Louvain, Belgium), A. Narath (Sandia),
R. Guertin (Tufts University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Studies of exchange enhancement D in metals and alloys have been extended to 200 kG. This approach involves a search for a field dependent susceptibility $\chi(B)$ of the metal or alloy which is predicted from theoretical calculations of the exchange enhanced Pauli paramagnetic susceptibility when D and B are large enough. The higher field measurements have reduced our estimate for D of Pd to a value ≤ 6 . Prior to this work estimates of D had ranged as high as 20 to 100. Measurements in Pd(Rh) alloys where $\chi_{\text{Pd(Rh)}} \approx 2 \chi_{\text{Pd}}$ show a directly observable field dependent χ above 150 kG, from which a value of D for the alloy and pure Pd can be estimated. An arc melter has been described for fabrication of high purity alloys of direct interest here.

Publications:

- MS 411 S. Foner, R. Doclo and E. J. McNiff, "The 'Pure' Pd Problem," J. Appl. Phys. 39, 551-552 (1 February 1968).
- MS 418 N. A. Blum and R. B. Frankel, "Magnetic Field Dependence of the Hyperfine Field at Fe in Dilute FePd Alloys," J. Appl. Phys. 39, 959 (1 February 1968).
- MS 426 S. Foner, "Magnetism in High Magnetic Fields," J. Appl. Phys. 39, 411-416 (1 February 1968).
- MS 415 J. I. Budnick, J. Lechaton, J. Wernick, S. Foner, E. J. McNiff, D. J. Kim and B. B. Schwartz, "Magnetic Properties of Pd-Fe Alloys," J. Appl. Phys. 39, 960 (1 February 1968).
- MS 419 B. B. Schwartz, D. J. Kim, R. B. Frankel and N. A. Blum, "Mossbauer Effect in Fe⁵⁷ in Copper and the Spin Compensated State,"

J. Appl. Phys. 39, 698-699 (1 February 1968).

7.0 Transport Studies of Local Moments in Dilute Alloys

Personnel: S. Foner, I. De Grave (University of Louvain, Belgium)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The field dependence of the magnetoresistance in dilute alloys of Cu(Fe), Cu(Cr), Fe(Rh), Pd(Fe), and related alloys has been examined for temperatures from 1.2 to 300°K and for fields to 200 kG. These experiments involve two aspects: 1) the attempt to observe the break-up of the spin-compensated state in those systems with a sufficiently low Kondo temperature; 2) the study of the saturation of a localized moment in a strongly exchange enhanced metal or alloy. The magnetoresistance is a simple tool for such studies particularly when a very low concentration of impurity is examined.

8.0 Magnetism in Nearly Ferromagnetic Metals and Alloys

Personnel: S. Foner, E. J. McNiff, D. J. Kim, B. B. Schwartz, Bucher (Bell Telephone Laboratories), I. De Grave (University of Louvain, Belgium), A. Narath (Sandia), R. Guertin (Tufts University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Theoretical and experimental studies of the magnetic moment versus field and temperature are being pursued in order to examine the approach to ferromagnetism in dilute alloys such as Pd(Fe), Pd(Co) and Pd(Ni) and in more concentrated systems such as Ni(Rh). To date our studies have employed high resolution moment measurements from 1.2 to 300°K and fields to 60 kG, and somewhat lower resolution studies to 200 kG. Evaluations of uniform and/or local exchange enhancements as well as band-filling effects are deduced by examination of the concentration and field dependence and detailed band calculations. The results are closely related to observations of neutron diffraction, NMR, Mossbauer effect, and many other

physical properties. Major problems near the magnetic phase transitions include clustering of magnetic impurities.

9.0 Magnetic Properties of Rare-Earth Single Crystals

Personnel: S. Foner, E. J. McNiff, J. J. Rhyne (Naval Ordnance Laboratory, White Oak, Maryland)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The magnetic moment of heavy rare-earth metals has been studied extensively at low temperatures. Extremely large anisotropies, the largest reported for any magnetic metal, have been observed in the basal plane of hexagonal Er and Ho. Measurements at 4.2°K and up to 200 kG show incomplete saturation except along the easy axis of these metals. The temperature dependence of magnetic phase transitions in heavy rare-earth metals is now being examined. Permanent deformations often are observed for fields as low as 60 to 100 kG in many of these materials.

Publications:

- JP 265 S. Foner and E. J. McNiff, Jr., "Very Low Frequency Integrating Vibrating Sample Magnetometer (VLFVSM) with High Differential Sensitivity in High d. c. Fields," Rev. Sci. Instr. 39, 171-179 (February 1968).
- JP 302 L. Holmes and M. Schieber, "Metamagnetism in Eu_3O_4 ," Phys. Rev. 167, 449-457 (10 March 1968).
- MS 409 J. J. Rhyne, S. Foner, E. J. McNiff and R. Doclo, "Rare Earth Metal Single Crystals I: High Field Properties of Dy, Er, Ho, Tb and Gd," J. Appl. Phys. 39, 892-893 (1 February 1968).
- MS 410 M. Schieber, S. Foner, R. Doclo and E. J. McNiff, "Rare Earth Metal Single Crystals II: Magnetic Properties of Tm, Eu, Sm, Yb," J. Appl. Phys. 39, 885-886 (1 February 1968).

10.0 High Temperature Superconductors

Personnel: S. Foner, E. J. McNiff, B. Matthias (Bell Telephone Laboratories and University of California at San Diego), E. Corenzwit

(Bell Telephone Laboratories)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Studies of critical field, H_{c2} , and critical temperature, T_c , for new NbGeAl alloys have been extended. RF loss as well as dc transverse magnetoresistance measurements of H_{c2} vs T are in good agreement and demonstrate that our rf methods measure H_{c2} accurately. The rf measurements allow studies of the NbGeAl alloy as cast without any mechanical treatment. The best NbGeAl alloys showed a $T_c = 20.7^\circ\text{K}$ which is the highest T_c yet obtained for any superconducting metal or alloy. This value of T_c has been confirmed by independent specific heat measurements (of Maita of Bell Telephone Laboratories). Measurements of H_{c2} vs T have been extended to 200 kG. We find that $H_{c2} = 200$ kG at 14°K demonstrating that these alloys would have many practical advantages over conventional superconducting materials. However, realization of this potential will require fabrication of high critical current carrying wire material.

11.0 High Field Resonance in Cerous Magnesium Nitrate

Personnel: H. C. Praddaude, R. O'Brien, S. Foner; S. J. Williamson
(North American Rockwell Corporation)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Cerous magnesium nitrate (CMN) is one of the classic materials for calibration and production of low temperatures down to the millidegree Kelvin region. The present low temperature scales, defined by magnetic temperatures of the CMN, involve assumptions concerning the magnetic properties of the dilute Ce^{3+} ion in this solid. Recent magnetic studies of Williamson and Cape have shown noticeable deviations of the magnetic moment of CMN from theoretical predictions. We have therefore examined the field dependence of the g -value in CMN with high resolution EPR spectroscopy from 35 to 125 GHz. A decrease in g -value (slightly less than 1% at 45 kG) has been measured which is in good agreement with calculations. However, this g -shift only accounts for part of the observed deviation of the

magnetization with field.

The g-value of a DPPH free radical marker, was also shown to be field independent to 45 kG during the course of this study. The properties of CMN in the millidegree temperature range are being studied by the Low Temperature Group (see preceeding section).

12.0 Mossbauer Effect Studies

12.1 Metals and Alloys

Personnel: R. B. Frankel, J. Chappert; N. A. Blum (NASA Electronics Research Center)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The external field dependence of the hyperfine field in Fe-Rh (1% Fe) at low temperature has been studied to obtain microscopic information on the saturation behavior of the Fe moment. In this system the moment is observed to decrease with decreasing temperature at low temperature, but there is no Kondo resistance anomaly. At $T \leq 4.2^\circ\text{K}$, as the external field is increased from 30 to 140 kOe, the net saturation hyperfine field at the ^{57}Fe nucleus is observed to increase in magnitude from -30 to -170 kOe. This behavior is similar to our observations of the external field dependence of the hyperfine field in dilute Fe in Cu, which we interpreted in terms of a spin-compensated state and its destruction by the external field. We conclude that although Fe-Rh does not exhibit the usual resistance anomaly, a spin-compensated state is formed at low T which is destroyed by an external magnetic field. Extrapolation of our data to 340 kOe, corresponding to $2.2\mu_B/\text{Fe}$ (from susceptibility measurements at high T), gives a value of 280 kOe for complete destruction of the bound state, or a Kondo temperature $T_K \approx 15^\circ\text{K}$.

The hyperfine interactions of ^{57}Fe in dilute Pd-Fe, Pd-Ni and Pd-Rh alloys have been measured in external magnetic fields. Our preliminary analysis indicates that those alloys which are ferromagnetic in high fields exhibit a field dependent contribution to the hyperfine field at high fields, whereas the paramagnetic alloys do not. We associate this behavior with the presence or absence of an exchange splitting of the host Pd conduction bands.

12.2 Non-metals

Personnel: R. B. Frankel, J. Chappert, A. Misetich; N. A. Blum (NASA Electronics Research Center)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The quadrupole splitting of ^{57}Fe nuclear levels in cubic MgO has been explained by Ham on the basis of a random strain model with slow relaxation, which lifts the 3-fold degeneracy of the Γ_{5g} spin-orbit triplet ground state. We observed that application of a small magnetic field (~ 1 kOe) induced magnetic hyperfine structure, indicating that for these fields, the electronic Zeeman splitting was much larger than the strain splitting. We have found that application of uniaxial stress to an MgO sample in a magnetic field results in quenching of the electronic angular momentum, when the stress splitting of the levels is comparable or greater than the Zeeman splitting. This manifests itself in a disappearance of the magnetic hyperfine splitting under large enough stress.

13.0 Laser Spectroscopy

13.0 Multiphoton Interband Absorption in Semiconductors

Personnel: J. Cherlow, B. Lax; N. A. Blum (NASA Electronics Research Center)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The experimental study of multiphoton absorption in small-gap semiconductors has been completed. It showed that the intermediate-state model did not explain the observed photoconductivity peaks. Therefore, a more complete calculation was undertaken and it revealed the intermediate-state model to be too weak to be observed. A completely different model involving a tunneling process was worked out and found to explain the data quite satisfactorily.

- JP 296 M. H. Weiler, M. Reine and B. Lax, "Theory of Multiphoton Magnetoabsorption in Semiconductors," Phys. Rev. 171, 949-958 (15 July 1968).
- JP 303 P. R. Schroeder, M. S. Dresselhaus and A. Javan, "Location of Electron and Hole Carriers in Graphite from Laser Magnetoreflexion Data," Phys. Rev. Letters 20, 1292-1293 (3 June 1968).

13.2 Luminescence Studies

Personnel: C. R. Pidgeon; S. Groves (Lincoln Laboratory); B. Lax

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

In a preliminary study of the excitation of silicon using a YAG laser a sharp spectral line was observed just below the band edge.

14.0 Magneto-Plasma-Phonon Interactions in Solids

Personnel: D. Cohn, R. Stimets, B. Lax

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Interferometric spectroscopy in the far infrared has been used to study the interaction between the plasma resonances in n-type semiconductors (InAs, GaSb and InSb) and the optical phonons by observing the anomalies in the dielectric constant as a function of frequency. Since the plasma frequency changes with the doping of the specimen and the resonances can be shifted and split by applying a large magnetic field, definitive experimental data was obtained by reflectivity which was analyzed by a Kramers-Kronig process. The frequency spectrum and scattering parameters from the line width of the spectra were compared with theory as a function of magnetic field.

15.0 Submillimeter Cyclotron Resonance

Personnel: K. J. Button, C. C. Bradley, A. Brecher, B. Lax

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The quantum effects in cyclotron resonance of holes in p-type semiconductors having degenerate valence bands are being studied experimentally and theoretically. Complete spectra showing the quantum effects have been obtained experimentally for germanium, indium antimonide and tellurium by using the HCN laser spectrometer at a wavelength of 0.337 millimeters. The spectra have been observed at a variety of temperatures between 10°K and room temperature in order to identify each spectral line unambiguously. The results showed that it was necessary to extend the quantum theory of cyclotron resonance. The theory has now been extended to include the interaction of the conduction band and the split-off valence band with the degenerate bands in both germanium and indium antimonide. A quasi-interband transition has been found to play a role in the case of indium antimonide.

Publications:

JP 312 K. J. Button, B. Lax and C. C. Bradley, "Quantum Effects in Cyclotron Resonance in p-type InSb," Phys. Rev. Letters 21, 350-352 (5 August 1968).

16.0 Infrared Magnetospectroscopy

16.1 Reflection and Electroréflexion Studies of Interband Magneto-Optical Transitions in Semiconductors

Personnel: C. R. Pidgeon; S. H. Groves (Lincoln Laboratory)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Reflection and electroréflexion studies of interband magneto-optical transitions in small band gap semiconductors have been completed in two areas. First, magnetoreflexion measurements in the temperature range 1.5°K to 80°K have led to a quantitative theoretical understanding of the zero band gap semiconductors of the grey tin type (specifically grey tin and

mercury telluride). Second, magnetoreflexion and electromagneto-reflection experiments at 1.5°K on III-V materials of the zinc-blende type (with particular emphasis on InSb) have given the first quantitative determination of the valence band parameters for the case of no inversion symmetry.

Publications:

- JP 272 Q. H. F. Vrehen, "Interband Magneto-Optical Absorption in Gallium Arsenide," *J. Phys. Chem. Solids* 29, 129-141 (January 1968).
- JP 297 C. R. Pidgeon and S. H. Groves, "Linear-k Valence Band Splitting in InSb," *Phys. Rev. Letters* 20, 1003-1007 (29 April 1968).
- MS 431 C. R. Pidgeon and S. H. Groves, "Low Temperature Electroreflectance Studies of Interband Magneto-Optical Transitions in HgTe," *II-VI Semiconducting Compounds, 1967 Internl. Conf.*, ed. D. G. Thomas (W. A. Benjamin, New York, 1967) 1080-1089.

16.2 Magnetopiezo-optical Studies of Germanium and the Lead Salts

Personnel: R. L. Aggarwal, U. Smith

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The high-sensitivity magnetopiezotransmission technique has been applied to the study of the indirect transition in germanium at low temperatures. This modulation technique has enabled us to observe Landau transitions over the whole energy range between the indirect and the direct energy gaps. The experimental data has been used to deduce the electron effective mass as a function of the energy relative to the band edge. The observed nonparabolicity of the conduction band has been compared with the results of the $\langle \vec{k} \cdot \vec{p} \rangle$ perturbation analysis.

The magnetopiezoreflexion study of the direct transition in germanium has been completed. This program has now been extended to include the lead salts. Preliminary results obtained for the as-grown p-type lead telluride show that the experimental data for the light mass transitions is in good agreement with Lax's two-band non-parabolic model.

16.3 Energy Band Studies in Uniaxially Stressed Semiconductors

Personnel: J. Halpern; F. Pollack (Brown University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The use of large uniaxial stress has proved to be a valuable tool for the analysis of semiconductor energy bands, particularly InSb where the degenerate valence bands complicate the spectrum of interband transitions observed in magneto-reflection. The stress separates the degenerate bands which permits identification of transitions and also provides a direct measurement of deformation potentials.

17.0 Adiabatic Demagnetization

Personnel: E. Maxwell; G. Zimmerman (Boston University); D. Kelland;
D. J. Abeshouse (Boston University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

In this work we have been concerned with the properties of cerous magnesium nitrate in the millidegree region of temperature. Temperatures in the range of 1 - 2 mK are obtained by direct adiabatic demagnetization of the salt from fields of the order of 95 kilogauss and temperatures of 1 K. Cerous magnesium nitrate (CMN) is of topical importance for two reasons. First, it is widely used as a magnetic thermometer in the millidegree region. Second, it exhibits a maximum in the magnetic susceptibility at about 2.5 mK which presumably signifies a cooperative transition. Apart from nuclear magnetic transitions it therefore represents the lowest temperature magnetic transitions so far known. Furthermore, it is a very dilute paramagnet in which exchange effects are essentially absent, the principal interactions being dipole-dipole in nature. A question of interest is whether the magnetic anomaly signifies a ferromagnetic or antiferromagnetic transition or neither. In order to answer this question we have been studying the frequency dependence of the susceptibility down to very low frequencies and its dependence on the applied superimposed dc magnetic field. We have also

observed some hysteresis effects in cyclic magnetization processes. Paramagnetic resonance studies of CMN are being carried out by the Transport and Resonance Group. (See Section 11.)

18.0 Ionic Mobility in ^4He in Magnetic Fields

Personnel: F. Dupre, M. V. Ricci (to September 1968); C. E. Chase (currently)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The purpose of this investigation is to determine the Hall mobility, μ_H , of a beam of positive or negative ions in liquid helium as a function of temperature and ion velocity, to determine the ratio of this quantity to the mobility, μ_T , measured by time-of-flight techniques, and to look for periodic discontinuities in μ_H as a function of velocity similar to those previously found in μ_T . By analogy with the theory of mobility in semiconductors, the ratio μ_H/μ_T should depend on the nature of the relevant scattering mechanism. Present observations with positive ions in the temperature range 0.7 - 0.8°K, where scattering of ions is predominantly by rotons, yield a ratio of unity. This suggests that rotons behave like point scatterers. Extension of the measurements below 0.6°K, where phonon scattering predominates, should disclose an increase in μ_H/μ_T to 1.18 if the semiconductor theory is applicable.

We have not yet observed periodic discontinuities in μ_H . However, since the corresponding behavior which has been observed in μ_T is at best somewhat elusive, this should not be construed as evidence that μ_H does not display such discontinuities. Much more detailed results will be required to answer this question satisfactorily.

19.0 Fluctuation Phenomena in Thin Film Superconductors

Personnel: R. Meservey; M. Ricci (University of Rome); E. Maxwell

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Measurements have been made of the critical current of aluminum thin films as a function of the temperature in the region just below the superconducting transition temperature, T_c . The thin films are in the form of narrow lines of different lengths. It has been found that near T_c the critical current decreases more rapidly with temperature than predicted by the Ginzburg-Landau theory giving a depression of T_c which increases as the films are made longer. This effect is presumably caused by fluctuations in the superconducting state near T_c .

Publications:

- JP 294 R. Meservey and L. Meyers, "Temperature Dependence of the Magnetic Field Periodicity in Flux Quantization Experiments," *Phys. Letters* 26A, 367-368 (11 March 1968).
- MS 334 B. B. Schwartz and E. E. H. Shin, "Flux Quantization and Metastable States in Superconducting Loop with no Josephson Junctions," *Proc. LT-10*, Vol. II-A (Moscow, 1967) p. 52.

20.0 Resonance Studies in Dilute Alloys

Personnel: H. C. Praddaude, R. O'Brien

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Anomalies in the transport properties of a variety of dilute alloys have received increased attention recently. Resistivity, thermoelectric power and specific heat among other transport properties have shown unusual behaviour as a function of temperature and magnetic field. The physical mechanism responsible for the anomalous behavior is not understood. We have begun a study of the resonance properties of Cu(Fe), Cu(Mn), Pd(Fe), etc. at 35 GHz using the reflection technique. The host-impurity coupling mechanism is reflected in the conduction electron spin resonance and in the resonance of localized moments giving rise to a coupled response. Study as a function of impurity concentration for different kinds of impurities provides a tool for examination of the interaction. The experiments are closely correlated with theoretical studies of wave propagation in metals in order

to assess the effects of different parameters on the resonances.

21.0 Cyclotron Resonance in Single Crystal Graphite

Personnel: H. C. Praddaude, R. O'Brien

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

High resolution cyclotron resonance studies in graphite provide information about band parameters impossible to determine otherwise. The solution of the transport problem, in the relaxation time approximation, has now been completed and preliminary computer results have been compared with experiments. New resonances were predicted by the calculations and have been subsequently observed when high-purity single crystal graphite samples with high-crystallographic perfection became available. The new structure is explained as arising from non-external pieces of the Fermi surface.

JP 298 M. Surma, "Mass Extremum Effect on the Cyclotron Resonance Line Shape in Gallium," Phys. Letters 26A, 562-563 (22 April 1968).

22.0 Ultrasonic Studies

Personnel: Y. Shapira; J. Zak; T. B. Reed (Lincoln Laboratory)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The propagation of ultrasonic waves near magnetic phase transitions was investigated. The study included the spin-flop transitions in the anti-ferromagnets MnF_2 and $\alpha\text{-Fe}_2\text{O}_3$, and the ferromagnetic transition in EuO . The spin-flop transitions of MnF_2 and $\alpha\text{-Fe}_2\text{O}_3$, which occur at high magnetic fields, were found to be accompanied by large anomalies in the ultrasonic attenuation and velocity. In EuO the attenuation at temperatures below the Curie point, in zero magnetic field was found to be higher than above the Curie point. The excess attenuation below the Curie point was removed by an external magnetic field, $H \gtrsim 4$ kG. The ultrasonic phenomenon observed

in all three materials can be explained in terms of antiferromagnetic and ferromagnetic domains.

Publications:

- JP 269 L. J. Neuringer and Y. Shapira, "Quantum Oscillations of the Velocity of Sound in Gallium," *Phys. Rev.* 165, 751-754 (15 January 1968).
- JP 295 Y. Shapira and J. Zak, "Ultrasonic Attenuation Near and Above the Spin-Flop Transition of MnF_2 ," *Phys. Rev.* 170, 503-512 (10 June 1968).
- MS 335 W. M. Whitney and C. E. Chase, "Ultrasonic Velocity and Dispersion in Liquid Helium II," *Proc. LT-10*, Vol. 1 (Moscow, 1967) p. 294-297.

23.0 High Field Superconductivity in V_3Ga and V_3Si

Personnel: L. Neuringer; Y. Shapira

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Measurements of the upper critical field H_{c2} have been completed on the high temperature superconductors V_3Ga and V_3Si . In these experiments there are several important points of departure from our previous work.

(1) We have investigated the effect of purity on H_{c2} for the high field superconductor V_3Si . (2) In the case of the single crystal V_3Si with resistivity ratio $= 37$ we have for the first time a pure, high field superconductor for which $\xi_0/\lambda > 1$. (3) V_3Ga and V_3Si are strong coupling superconductors. (4) Knight shift data are available for these materials, and therefore we have direct knowledge of λ_{so} , the frequency of spin-flip scattering events. Thus λ_{so} can no longer be taken as an adjustable parameter. (5) The measured upper critical field of V_3Si is anisotropic. In the case of pure V_3Si we have been able to estimate from the H_{c2} vs T data several important normal state electronic parameters such as the Fermi velocity and the scattering time. A paper is now in preparation which will confront the aforementioned new features with the diverse theories for these effects.

Publications:

MS 333 S. J. Williamson, "Effect of Paramagnetism on Upper Critical Fields of High Field Superconductors," Proc. LT-10, Vol. II-A (Moscow, 1967) pp. 470-473.

24.0 Piezo-Magnetoresistance in Degenerate Semiconductors

Personnel: L. Neuringer; F. Pollak (Brown University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The effects of large static compressive uniaxial stress on the magnetoresistance of degenerate n- and p-type silicon and n-type germanium are being investigated up to 150 kG. These investigations are aimed at understanding the scattering mechanism responsible for the negative magnetoresistance observed in these materials. The negative magnetoresistance increases with stress up to $2 - 3 \times 10^9$ dynes-cm⁻², after which it saturates. In addition, stresses above 2×10^9 dynes-cm², applied along [111], Shubnikov-de Haas oscillations were clearly observed in As and P-doped germanium ($n \sim 2 \times 10^{18}$ cm⁻³). These periods are in good agreement with calculations based on a simple one-band model.

25.0 Quantum Limit Transport Phenomena

Personnel: L. Neuringer; L. Kaufman (Tufts University)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

A He³ cryostat operating in the continuous mode has been assembled and tested in the presence of ambient magnetic fields up to 150 kG. With the aid of a Nb₃Sn ribbon superconducting shield we have been able to achieve excellent temperature regulation in the continuous mode at 0.5°K in the presence of a swept magnetic field, and in the single shot made to 0.40°K. Experiments on the magnetoresistance and Hall coefficient of n-InSb and n-InAs have been carried out, to check various predictions concerning the

magnetic freezeout phenomenon.

26.0 Spin Wave Side Bands

Personnel: A. Misetich; R. E. Dietz, (Bell Telephone Laboratories)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

A number of recent papers have been concerned with the properties of the optically excited states of MnF_2 , particularly those states belonging to the lowest $^4T_1$ configuration. These transitions are narrow zero magnon lines and magnon side bands. To calculate the shapes of the magnon side bands a Frenkel exciton representation has been assumed for these excited states. In recent experiments we have demonstrated that the excitons must have an energy dispersion, if any, of less than 1 cm^{-1} . However, in a later experiment we have proved that there is a thermodynamic distinctness of the zone center and zone boundary exciton states (responsible for the narrow lines and the magnon side bands respectively).

Publications:

- MS 408 A. Misetich and R. E. Dietz, "Role of Exciton Dispersion and Exciton Magnon Interactions on the Shape of Magnon Side Bands in Stressed MnF_2 ," J. Appl. Phys. 39, 1145 (1 February 1968).
- MS 432 A. Misetich, R. E. Dietz and H. J. Guggenheim, "Spin Wave Side Bands of Localized Excitons," in Localized Excitations in Solids, Ed. R. F. Wallis (Plenum Press, New York, 1968) pp. 379-385.
- MS 455 R. E. Dietz and A. Misetich, "Optical Studies of Localized Magnons and Excitons," in Localized Excitations in Solids, Ed. R. F. Wallis (Plenum Press, New York, 1968) pp. 366-378.
- JP 315 A. Misetich, R. E. Dietz, A. E. Meizner and H. J. Guggenheim, "Observation of a Thermodynamic Distinction Between Brillouin Zone Center and Boundary Exciton States in MnF_2 ," Phys. Rev. Letters 21, 1067-1070 (7 October 1968).

27.0 Calculation of the Magnetic Susceptibility of Pd

Personnel: A. Misetich; R. E. Watson (Brookhaven National Laboratory)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Some preliminary results for the unenhanced paramagnetic spin susceptibility $\chi_o(q, \omega)$, have been obtained for Pd metal. Band structure effects have been accounted for utilizing the pseudopotential scheme of Hodges, Ehrenreich and Lang. The contribution of the fifth band (which is responsible for the "jungle gym" Fermi surface) was inspected and compared with the total susceptibility. Spin orbit quenching of band spin character affects the results.

28.0 Magnetic Measurements Employing an AC Temperature Technique

We have measured $\partial M / \partial T$ for a series of Pd-Fe alloys in fields up to 30 kG at temperatures from 1.2 to 30°K. The samples have Curie temperatures ranging throughout this interval so that we have studied the ferromagnetic, transition region, and paramagnetic phases.

28.1 $\partial M / \partial T$ Measurements in Paramagnetic Pd-Fe Alloys

Personnel: R. R. Oder

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

In the paramagnetic phase, comparison of $\partial M / \partial T$ with simple molecular field models has yielded saturation moments per iron impurity in rough agreement with the results of independent magnetization measurements. However, g and J values, independently determined in a forced Brillouin fit to $\partial M / \partial T$, have shown strong (T, H) dependences unobserved in magnetization measurements. We have concluded that the low field magnetization of these exchange enhanced alloys is not Brillouin-like in an external magnetic field.

28.2 Spin Waves in Dilute Ferromagnetic Alloys

Personnel: R. R. Oder, D. J. Kim

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Recently much new experimental data on the spin wave spectrum of Pd-Fe systems has been obtained, but understanding of this problem at the present stage is very poor. For instance, the measured spin wave frequency is more than 10 times bigger than the theoretically estimated value. More remarkable is the effect of the external magnetic field on the spin wave spectrum which is quite different from that which one would predict from the usual picture of a spin wave using the Heisenberg model.

We are applying the oscillating temperature developed earlier in this laboratory in this problem and studying especially the magnetic field dependence of the spin wave spectrum in various temperature regions. At the same time a theoretical explanation to account for the data quantitatively is being attempted.

Publications:

MS 412 R. R. Oder, "Application of a Temperature Oscillation Method to Thermo-Magnetic Studies of Magnetic Phenomena at Low Temperatures," J. Appl. Phys. 39, 848 (1 February 1968).

29.0 Theory of Electron Interaction in Magnetic Metals

Personnel: D. J. Kim

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

An effective interaction between conduction electrons has been obtained by eliminating the exchange interaction between conduction electrons and localized spins in metals both in the paramagnetic and spin-ordered state. In the paramagnetic state the effective electron interaction is mediated by the flipping motion of the localized spin under the action of the local field and the electron interaction derived is of an exchange type and repulsive in the vicinity of the Fermi surface. On this basis we have shown that the observed ferromagnetism in dilute alloys like Fe in Pd may be understood from the large enhancement of the conduction-electron susceptibility.

This study has been extended to a spin-ordered system such as a ferromagnetic rare-earth metal below the Curie temperature. The effective interaction obtained is of a form of repulsion between electrons of opposite spins at the same atomic site in the vicinity of the Fermi surface. The electron self-energy due to this effective electron interaction has been calculated for a simplified model and we have assessed the possibility of an appreciable enhancement of the electronic specific heat in rare earth metals.

Publications:

- JP 267 D. J. Kim, "Electron Interaction in Rare Earth Metals," Phys. Rev. 167, 545-550 (10 March 1968).
- MS 414 D. J. Kim, "Enhanced Effective Exchange Interaction due to Localized Spins in Dilute Alloys and Rare-Earth Metals," J. Appl. Phys. 39, 702-703 (1 February 1968).
- MS 416 R. E. Watson and A. J. Freeman, "Local Moment Conduction Electron Exchange Coupling and RKKY Spin Densities in Metals," J. Appl. Phys. 39, 1100 (1 February 1968).
- MS 417 D. E. Ellis and A. J. Freeman, "Model Calculations for the Study of Direct and Superexchange Interactions," J. Appl. Phys. 39, 424-426 (1 February 1968).

30.0 Neutron Scattering in Ferromagnetic Dilute Alloys

Personnel: D. J. Kim and B. B. Schwartz

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

From measurements of the neutron elastic diffuse scattering in ferromagnetic dilute alloys one obtains information concerning the spatial distribution of the conduction electron spins as well as the spin on the impurity atom. The alloys of Fe or Co in Pd are especially interesting since the conduction electron spin polarization has been shown to have a very long range, $\sim 10 \text{ \AA}$. This exceedingly long range of magnetic perturbation due to a magnetic impurity is attributed to the large exchange enhancement of the Pd matrix and the interatomic nature of the electron-electron interaction. Another interesting aspect of the problem, although it has received less attention is that the range of conduction electron spin polarization around a

magnetic impurity decreases sharply with increasing concentration of magnetic impurities, i. e., the neutron scattering experiment shows that increasing the Fe or Co concentration from ~ 0.5 to 4.0 atomic percent reduces the range from 10 to 1 Å.

A new basis for the analysis of the neutron elastic diffuse scattering data in ferromagnetic dilute alloys has been formulated as follows: In exchange enhanced metals, the spatial extent of the spin polarization around an impurity disturbance may decrease sharply as the spin splitting of the host matrix increases. Increasing the impurity concentration in dilute ferromagnetic alloys leads to an increase in the spin splitting of the host matrix bands. We have derived an expression for the conduction electron spin polarization which self-consistently includes the concentration dependence of the spin splitting of the host matrix and accounts for the sharp concentration dependence observed in the neutron scattering experiments. In analyzing the neutron scattering experiments we have shown that simple parabolic bands with 0.36 holes/atom are a very poor approximation for the 3d hole bands of Pd. This is in agreement with recent band calculation results. Further, the falloff with q of the susceptibility function for the actual band is expected to be significantly more rapid than for a parabolic band.

Publications:

JP 289 D. J. Kim and B. B. Schwartz, "Spin Polarization Around a Localized Magnetic Impurity in a Magnetized Field," Phys. Rev. Letters 20, 201-204 (29 January 1968).

JP 319 D. J. Kim and B. B. Schwartz, "Neutron Scattering in Ferromagnetic Dilute Alloys," Phys. Rev. Letters 21, 1744-1747 (23 December 1968).

31.0 Ultra-High Critical Field in Superconductors with Magnetic Impurities

Personnel: B. B. Schwartz; L. W. Gruenberg (Center for Materials Science and Engineering and Department of Electrical Engineering)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

Recently the effect of an internal molecular field, due to ordering among magnetic impurities, on the external critical field for a superconductor

whose upper critical field is limited by Pauli spin paramagnetism has been considered. One obtains the unusual result that under appropriate conditions the critical field at low temperature can decrease with decreasing temperature. This decrease in the critical field at low temperature has been observed in $\text{La}_{3-x}\text{Gd}_x$ and in $\text{La}_{1-x}\text{Gd}_x\text{Sn}_3$.

A superconductor containing magnetic impurities which couple antiferromagnetically to the conduction electron spin, however, offers the additional possibility of ultra-high critical fields. The internal field produced by the impurities (whose value can be made very large, $\sim 10^6$ gauss) can be cancelled by an external field leading to no net field acting on the conduction-electron spin. Thus the alloy can regain its superconducting properties in the presence of a very high field. To observe this effect the impurity spin must couple antiferromagnetically to the host electron spins. A light metal superconductor where spin orbit effects are small can be used in the form of a very thin film specimen or a type II superconductor with a large ratio of $H_{c2}^*(0)$ the upper critical field in the absence of Pauli spin paramagnetism to $H_p(0)$, the Pauli paramagnetic field. Since the anomalous lower critical field curve also follows from our arguments, the study should include those specimens which display the unusual low temperature decreasing critical field behavior.

32.0 The Dynamics of Electrons in Solids in External Fields

Personnel: J. Zak (Dr. Zak was a Visiting Scientist at the Laboratory.

He is carrying on this work as a Visitor at Northwestern University.)

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The kq -representation of the motion of an electron in a periodic potential plus a uniform electric or magnetic field developed here previously was applied to several outstanding theoretical problems. The existence of the Stark ladder in solids in electric fields was considered. It was shown that, contrary to prevailing opinion in the literature, no Stark ladder follows from the existing theory. In another application of the kq -theory, the Bloch theory of an electron in an external field has been reformulated. It is shown that the quasimomentum is a purely quantum mechanical quantity with no classical analog. For a Bloch electron in a magnetic field a set of magnetic Bloch functions are introduced. These functions are shown to

behave according to the magnetic translation symmetry, and it is for this reason that they form the proper set for expanding the solution of a Bloch electron in a magnetic field. By using these functions the effective Hamiltonian is developed in a straightforward way to any order in magnetic field.

Publications:

JP 291 J. Zak, "Dynamics of Electrons in Solids in External Fields,"
Phys. Rev. 168, 686-695 (15 April 1968).

JP 299 J. Zak, "Stark Ladder in Solids?", Phys. Rev. Letters 20, 1477-
1481 (24 June 1968).

33.0 Instrumentation for High Magnetic Field Research

33.1 Low Temperature Thermometry in Magnetic Fields

Personnel: L. Neuringer, Y. Shapira, L. Rubin, A. Perlman

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

The purpose of this program is to provide sufficiently accurate measurements of the magnetic field-dependent characteristics of various temperature measuring systems over the temperature range from 2°K to room temperature. With the information it should then be possible to choose an optimum system for a particular temperature range in fields as high as 150 kG. For example, it is well known that at 10°K , a germanium RT (resistance thermometer) has a higher sensitivity than a carbon RT, and that at 40°K , a platinum RT has a higher sensitivity than a germanium RT. However, if, as suspected, the magnetoresistance of the latter of each pair is much smaller than the former, this could more than offset the sensitivity difference.

During 1968, a complete apparatus for making these measurements in a 150 kG magnet was assembled and tested. It employs a constant-volume gas thermometer as a null detector for temperature, along with a suitable cryogenic system capable of covering the $2 - 300^{\circ}\text{K}$ temperature range. The measurement of the thermometers themselves are performed on a specially designed semi-automatic system. We have completed a study of the trans-

verse and longitudinal magnetoresistance of 1/10 watt and 1/4 watt Allen-Bradley carbon resistors as a function of temperature between 1.8 - 18°K in magnetic fields up to 150 kG. Ten different resistors having nominal values at room temperature of 47, 100, 220 ohms were investigated. It was found that the magnetoresistance at low temperatures is small and reproducible for a given resistor. Furthermore, it is the same for resistors of the same nominal value at room temperature. Thus, once the magnetoresistance of a given resistor has been measured at a certain temperature, then the magnetoresistance of any other resistor with the same nominal value at room temperature can be estimated to good accuracy and subtracted out. The smallness of the magnetoresistance of Allen-Bradley carbon resistors and the fact that it can be estimated from data on other resistors of similar nominal value make these thermometers useful in high magnetic fields. A paper for publication in Rev. Sci. Instr. is now being prepared.

33.2 Improved Techniques for Detecting Low Light Levels

Personnel: L. Rubin. W. Lutts

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

In the spectral region 0.4 - 1.1 microns, it is well known that photomultiplier (PM) tubes are the best available detectors for low light levels. A great deal of information has been published on the relative importance of such parameters as photocathode and electron multiplier type and design cooling, stray fields, image size, etc. Comparatively little has been reported (and that only recently) on new signal processing methods and techniques for operating on the PM tube output. It is the purpose of this program to compare the three most promising methods, as used with three different tube types.

Equipment has been assembled and tested and measurements have recently begun on standard 10-stage, 1 inch diameter S-1, and 14-stage, 2 inch, S-20 PM tubes. Also available is one of the new channel-multiplier, limited aperture PM tubes that is expected to provide greatly superior performance in certain conditions. A new type of low level source (a phosphor excited by radioactive Kr gas) is being used with neutral density filters to provide an adjustable, stable, reference level.

The three methods of measurement are: 1) the popular chopped beam-

phase sensitive detector scheme; 2) single photon counting, using the pulse-shaping amplifiers and pure height analyzers of the scintillation-counting nuclear physicists; 3) the recently announced shot-noise measurement method, which makes use of cross-correlation techniques to implement what may be an important discovery in the field of measurement technology.

34.0 Kinetic Inductance Measurements of Linear Superconductors

Personnel: P. Tedrow, R. Meservey

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

A technique for measuring very small inductances ($L \approx 10^{-13}$ h) has been developed in order to measure the inductance associated with the mass of the supercarriers in a linear geometry. This technique has been successfully used with wires and thin film meander lines to determine the carrier concentration and penetration depth of tin. Since the carrier concentration is a rapid function of temperature (near T_c) and of magnetic field (near H_c), these meander lines were found to be sensitive temperature and magnetic field transducers. This simple technique has been also used to detect quantized flux changes in superconducting loops and is competitive in sensitivity with other more complex techniques.

35.0 Calorimetric Measurements Employing an AC Temperature Technique

Personnel: R. R. Oder

Sponsorship: Air Force Office of Scientific Research, F44620-67-C-0047

Research Report:

We have extended the ac temperature technique to measurements of the temperature and field dependence of the heat capacity, $C(T, H)$, in high magnetic fields where we are studying 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 $Ni_{.625}Rh_{.375}$ observed by others and attributed to critical spin fluctuations. When measurements are made to

100 kG we find that the anomaly is removed and the heat capacity is well represented by $C \sim \gamma T + \beta T^3$ in the interval $2 \leq T \leq 8^\circ\text{K}$.

In a control experiment we have measured $C(H, T)$ for 5 - 9's pure indium and have established that the anomaly observed in the Ni-Rh measurements is independent of the apparatus. Our determination of C and of the superconducting transition temperature for indium are in excellent agreement with accepted values.

36.0 Cooperative Programs

More than half of the magnet operating hours in 1968 were used by visitors. Brief descriptions of some of their programs are given here.

Professor P. S. Pershan of Harvard and a graduate student, P. Eisenberger, measured the effective mass of the polaron in rare-earth doped CaF by the cyclotron resonance technique. Professor L. C. Robinson of Yale operated a cyclotron resonance maser over the wavelength range 2.47 mm to 725 μm . Dr. R. Kaiser of the AVCO Corporation Space Systems Division measured the effect of high magnetic fields on the viscosity of stable dispersions of subdomain size magnetite particles in a liquid carrier. The variable viscosity properties of these fluids may have important practical applications. The MIT group lead by Professor A. Javan and Professor M. Dresselhaus used their precise laser techniques for magnetospectroscopic studies of bismuth, antimony, InSb and pyrolytic and single crystal graphite. In graphite the carriers at the K point of the Brillouin zone, always thought to be holes, were found to be electrons. Dr. J. Korving of the Kammerlingh Onnes Laboratory of the University of Leiden completed a year and a half study of the influence of high magnetic fields on the viscosity of polyatomic gases. Considerable new information on momentum transfer and collision cross sections between molecules was obtained. The Group from the Naval Aerospace Medical Institute at Pensacola exposed squirrel monkeys to fields up to 95 kilogauss and observed inhibitory effects and vomiting. These studies on the lower primates are preliminary to a planned study of the effect of strong magnetic fields on man. Professor Sellmyer and his students in the MIT Metallurgy Department have continued their studies of the Fermi surface in metals and alloys by measurement of the high field magnetoresistance. Materials studied include lead, AuSb_2 , PbIn alloys, and transition metal-aluminum alloys. Dr. H. Belson of the Naval Ordnance Laboratory has made the first complete measurement and analysis of oscillatory magnetostriction in a multivalley semiconductor. Professor J. A. Marcus of Northwestern University and Dr. W. A. Reed of Bell Telephone

Laboratories extended their study of galvano-magnetic effects in chromium to 205 kilogauss. Dr. H. Roth and co-workers at the NASA Electronics Research Center continued their transport studies of heavily doped silicon. Dr. E. L. Wolf and co-workers from Eastman Kodak Co. investigated magnetic-field effects on tunnelling in metal-semiconductor junctions. Professor J. Steinfeld and his student of the MIT Chemistry Department examined the magnetic quenching of fluorescence in iodine vapors. Groups from the Franklin Institute, AVCO-Everett Research Laboratory, RCA Laboratories, Air Reduction Corp., Supercon Division of Norton Co., Research Institute for Metals, Tokyo, and the MIT Metallurgy Department used Laboratory magnets for the study of high field 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
 W. G. Denhard, Associate Director
 M. S. Sapuppo, Associate Director
 Dr. E. B. Dane, Deputy Associate Director
 A. P. Freeman, Deputy Associate Director
 E. J. Hall, Associate Director

Staff Members Participating in Materials Research:

Dr. S. Allen
 G. Augeri
 A. R. Calabrese
 A. C. Edwards
 C. S. Elder
 Mrs. L. K. Garfinkle
 C. H. Hanson
 W. H. Keating
 G. F. MacNeill
 J. K. McEwen
 R. L. Morey
 J. L. Nelson
 J. R. Palmieri
 M. Roberts
 B. Rockower
 H. Rowe
 R. J. Schiesser
 Dr. J. R. Stemniski
 K. A. Taylor

Sponsorship:

Listed under subheadings

REPORT ON RESEARCH ON MATERIALS AT THE
INSTRUMENTATION LABORATORY

1.0 Fracture Mechanisms in Oceanic Cable

Personnel: Ronald L. Morey

Sponsorship: Woods Hole Oceanographic Institute

Research Report:

Failure mechanisms of various types of wire cable are under investigation. The mode of failure is being related to loading, wire configuration and past history of cable.

Publication:

H. D. Bertaux, R. Mitchell, E. A. Capadona, and R. L. Morey, "Experimental Evidence on the Modes and Probable Causes of a Deep-Sea Buoy Mooring Line Failure" Transactions of the 4th Annual M.T.S. Conference 1968.

2.0 Synthesis of High Density Gyro Fluids

Personnel: Bertram Rockower

Sponsorship: NASA Contract, NAS 9-4065 (Task Order No. 35)

Research Report:

The objective of this effort is to synthesize a fluid that has a minimum density of 3 grams/cc and a viscosity of approximately 2400 cps at 137°F. A high density gyro flotation fluid is desirable in that it makes possible the design of smaller instruments or instruments with greater angular momentum.

Research work on this project was performed by the M & T Chemical Co., Rahway, N. J. During the past year a fluid has been isolated from the class of antimony - stabilized halophosphazene polymers with a density of

2.93 gm/cc and a viscosity at 137°F of 2000 cps. The fluid behaves in a Newtonian manner; is essentially non volatile; does not conduct electricity and exhibits a pour point of 18°C. Preliminary compatibility tests have shown the fluid to be non-corrosive towards the common materials of construction of the gyro. A final report summarizing the work accomplished by the M & T Chemical Co. was written on 9-6-68.

3.0 Studies of Materials for Gas-Lubricated Gyro Bearings

Personnel: H. Rowe

Sponsorship: NASA/MSC Contract NAS 9-4576 (Subcontract 349)

Research Report:

A program was conducted to develop and evaluate an improved aluminum oxide ceramic gas-bearing material. The material for evaluation consisted of a fine-grain size, hot-pressed aluminum oxide, with and without a vapor-deposited coating of the same material. Evaluation included extended start-stop testing as well as slew testing to touchdown. Both material combinations exhibited superior wear characteristics to the conventional cold pressed and sintered aluminas previously tested, but failed to provide a high-speed touchdown survivability for the design evaluated.

Publications:

Henry Rowe, "An Investigation of Methods to Improve the Wear Resistance of Gas-Bearing Ceramic Materials", Trans. ASME Journal of Lubrication Technology Vol. 90, Series F, No. 4 October 1968, pp. 829-840.

4.0 Newtonian Behavior of Damping Fluids

Personnel: Dr. J. R. Stelmiski

Sponsorship: Air Force Contract AF 04(694)-999; Navy Contracts N00030-66-C-0189 and N00030-68-C-0154

Research Report:

Damping fluids presently used in inertial measuring units are telomers of bromotrifluoroethylene of relatively short chain length. Because of the processing technique, it is believed that the fluids used contain telomers of various chain lengths. Polymer systems of unequal chain length are known to exhibit non-Newtonian behavior. Non-Newtonian behavior in damping fluids is an extremely undesirable effect. Therefore, an attempt was made to describe this property of damping fluids with a power-law relationship.

The apparent bulk viscosities of several fluids were measured with a ball and cup viscometer and capillary viscometers over the shear rate range of 0.02 to 4 sec^{-1} . Plots of $\log$ (shear stress) versus $\log$ (shear rate) gave straight lines with slopes very close to one. This indicates that these fluids demonstrate Newtonian behavior over the given range of shear rates as the basic definition of Newtonian behavior is complied with.

Using Cannon-Ubbelohde semi-micro dilution capillary viscometers, the viscosities of dilute solutions were measured. From this data, intrinsic viscosities were calculated and it was determined by using this technique that the fluids appeared to be Newtonian within the sensitivity of the apparatus used.

A mathematical treatment of the theory as applied to this program was also undertaken.

It can be concluded from the data obtained from both the ball and cup, as well as the capillary viscometers, that the damping fluids are Newtonian within the experimental accuracy of the testing apparatus.

5.0 Permanent Magnet Stability

Personnel: Dr. J. R. Stelmiski

Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

It has been determined that instabilities in the magnitude of the flux density of the Alnico V alloy, used as permanent magnets in inertial measuring units, can be attributed to improperly controlled processing procedures during fabrication.

Based on the metallurgy of the standard processing for Alnico V, a specification for more careful control of processing was recommended. Of

primary interest in this recommendation are the composition and the procedures for heat treatment and stabilization of the alloy. These recommendations have been taken under advisement.

6.0 Disaccommodation in Ferrites

Personnel: Dr. J. R. Stelmanski

Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

Disaccommodation as applied to ferrite materials is defined as the decrease in permeability of the magnetic material with time after some change in the external field acting on the material. Inertial measuring units designed by the MIT Instrumentation Laboratory exhibit a degree of error which has been traced, in part, to disaccommodation effects in a ferrite component in the instrument.

A literature investigation was undertaken to determine the causes of disaccommodation in ferrites. This phenomenon was studied extensively during the early 1960's and was apparently found to be caused by the diffusion of cation vacancies in the lattice of the ferrite. Such vacancies occur when the ferrite contains more than the stoichiometric amount of oxygen.

An experimental program has been initiated to synthesize ferrites having low disaccommodation with no sacrifice of the other properties. This program is being pursued by an MIT Senior Metallurgy student under the direction of Institute and Instrumentation Laboratory personnel. The principal technique involved in this approach will be sintering the material in a controlled atmosphere. Reducing conditions which will remove excess oxygen in the lattice are expected to minimize the disaccommodation effects.

7.0 Analysis of Contamination in Gyroscopes by Electron Beam Micro-Analysis

Personnel: Dr. J. R. Stelmanski

Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

Analysis of microscopic contamination of gyro components continues to be a problem. However, it has been shown that electron beam microprobe analysis is a very useful tool in determining the composition of metallic contaminants and contamination-containing elements with atomic numbers greater than 7.

8.0 Investigation of Gyro Damping Fluids by Gel Permeation Chromatography; A Study of the Correlation Between GPC and Thermal Diffusion

Personnel: Dr. J. R. Stemniski, Mrs. L. K. Garfinkle

Sponsorship: Air Force Contract AF 04(694)-999; Navy Contract N00030-66-C-0189; NASA Contract NAS 12-569

Research Report:

The gel permeation chromatography program has been directed primarily toward determination of molecular weight distribution of bromotrifluoroethylene telomer damping fluids. The apparatus used is a Waters Associates Model 200 gel permeation chromatograph. Conditions for optimum separation of these mixtures have been determined and were reported at the Sixth International Seminar on Gel Permeation Chromatography at Miami Beach, Florida in October 1968. Using these conditions, it was found that analytical interpretation of the resulting chromatograms could be made with speed and reliability.

The program has now been extended from the analytical range to the semi-preparative range. The apparatus has been modified to include the new one-inch gel-packed columns which will allow separation and collection of larger samples which can subsequently be subjected to independent analysis. Characterization of the components of the mixture will allow the preparation of a composite chromatogram. Further analysis may then permit the generation of a "standard" chromatogram.

An attempt is being made to mathematically reduce the chromatograms to obtain a corrected curve. This work is in a preliminary stage, but the results are expected to eliminate variables which may cause erroneous interpretation of "raw" chromatograms.

Using the analytical conditions which proved very successful in preliminary investigation of telomer fluids, an evaluation of thermal diffusion

fractions was made. The American Society for Testing and Materials Committee on Gyro Fluids and Interacting Materials has performed Round-Robin testing on the thermal diffusion of two typical gyro damping fluids. The fractions were analyzed by GPC and distinctions were evident. Since thermal diffusion is the method currently used to determine molecular weight distribution in damping fluids, a correlation between GPC and thermal diffusion would permit the substitution of GPC for thermal diffusion. This would be extremely desirable since GPC is fast, accurate, and reliable.

Publication:

J. R. Stelmiski, "Determination of Molecular Weight Distribution of Bromotrifluoroethylene Telomer Fluids by Gel Permeation Chromatography", Sixth International Gel Permeation Chromatography Seminar, Miami Beach, Florida, October 1968.

9.0 Accelerometer Fluids

Personnel: Dr. J. R. Stelmiski

Sponsorship: Air Force Contract AF 04(694)-999; NASA Contract NAS 12-569

Research Report:

In addition to fluids possessing high density and high viscosity, there exists a need for fluids with high density and very low viscosity (in the range of one centipoise). These fluids must possess the same properties as the high viscosity fluids, in addition to being compatible in electrical environments.

The currently used fluid, FC-43 (3M Company), has a density of about 1.88 gm/cm^3 . Improvements in instruments again require a search for higher density materials.

Several candidate fluids in the density range of 2.6 gm/cm^3 are being considered. In addition, several large chemical companies have indicated that they may have fluids which would fill the requirement. However, because of the patent situation, no comment can be made at this time concerning these candidates.

10.0 Gyro Damping Fluids

Personnel: Dr. J. R. Stelmiski

Sponsorship: Navy Contract N00030-66-C-0189

Research Report:

Improvements in inertial measuring units have made the need for improved damping fluids more critical. The presently used telomeric fluids possess several undesirable properties associated with the fact that they are blends of varying chain length telomers. Obtaining a single species fluid would eliminate the problems of thermal diffusion effects, change in composition due to volatility, and problems associated with minute degree of non-Newtonian behavior.

Peninsular ChemResearch Inc., Gainesville, Florida, under Navy sponsorship, is attempting to synthesize a singular molecular species fluid with densities in the range of 2.4 gm/cm^3 and higher. This work is in a preliminary stage and a detailed progress report is expected to be published within a short time.

In addition to the chemical and physical problems associated with the presently used damping fluids, the fact that these fluids are manufactured by only one company is most undesirable. This is further complicated by the fact these fluids are considered proprietary and no information regarding the method of preparation is ever revealed by the source. The method of preparation is not protected by a government patent.

Peninsular ChemResearch Inc., again under Navy sponsorship, has been awarded a subcontract to prepare a replacement fluid of the bromo-trifluoroethylene type presently used in instruments. This contract has just been awarded, thus no progress can be reported at this time.

11.0 Determination of the Unsaturation in Damping Fluids Using the Technique of Microhydrogenation

Personnel: Dr. J. R. Stelmiski, Mrs. L. K. Garfinkle

Sponsorship: Air Force Contract AF 04(694)-999; Navy Contract N00030-66-C-0189; NASA Contract NAS 12-569

Research Report:

Chemical unsaturation in damping fluid is a deleterious property since these sites of unsaturation are susceptible to oxidation, the products of which are corrosive to reactive components. Damping fluids should be as saturated as possible in order to reduce the possibility of oxidation. The method of detecting unsaturation in damping fluids involves the use of potassium permanganate solution, a somewhat classical test for chemical unsaturation in certain systems. However, in fluorocarbon chemistry and especially as related to damping fluids, the test is less than reliable.

Microhydrogenation has been demonstrated to be useful in hydrocarbon systems. By means of a catalytic hydrogenation, this method allows analyses of 5×10^{-5} mole of unsaturation with an accuracy of 0.5 to 1.0 percent. Levels as low as 5×10^{-6} mole have been detected. This technique seemed quite appropriate for the program and a study using a Brown² Micro Hydro-Analyzer was begun. After several attempts, a successful generation of hydrogen was achieved. However, repeated trials resulted in an absorption of greater than the theoretical amount of hydrogen. It was concluded that the more labile halogens, such as bromine and chlorine which are contained in the damping fluid telomer, were being replaced in addition to saturation of the double bonds present. No further work was conducted in this area with this method after arriving at this conclusion.

12.0 Damping Fluid Properties at Low Temperatures

Personnel: Dr. J. R. Sterniski

Sponsorship: LRL Contract AT (30-1)-3911

Research Report:

Because inertial measuring units are sometimes required to perform at extremely low temperature, a program to determine the pour points and cloud points of viscous damping fluids was undertaken.

Using a Weber Environmental Testing Chamber capable of reaching temperatures as low as -100°F , a series of fluids with viscosities ranging from 179 to 5793 centipoises was subjected to incremental temperature reduction. Most high viscosity fluids (viscosity > 1000 cp) exhibited pour points in the range of 30° - 40°F . All fluids, with one exception, went through glass transition states and therefore did not have cloud points as defined by

the American Society for Testing and Materials. All fluids tested did, however, demonstrate a cracking point. This ranged from -25°F to below -100°F for the least viscous fluid tested. It appears from these results that the useful fluid range of the materials used is above $+40^{\circ}\text{F}$.

13.0 Determination of Coefficient of Thermal Expansion

Personnel: J. R. Palmieri

Sponsorship: Air Force Contract F33615-68-C-1155

Research Report:

Accurate values for coefficient of thermal expansion over appropriate temperature ranges are required by designers of precision instruments. Since chemical composition, mechanical working history, and thermal history of a material may influence its thermal expansion characteristics, a capability has been established at MIT/IL for determining CTE for instrument components in forms as close to finished design as desired.

The technique consists of applying electrical resistance foil strain gages to the specimen. The part is heated in a circulating oil bath whose temperature is measured by a calibrated mercury-in-glass thermometer. The temperature range of interest is usually room temperature to 212°F . The apparent strain data is the sum of the thermal expansion of the material plus the temperature coefficient of resistivity effects of the strain gage material. Since the latter is supplied by the gage manufacturer or may be determined by applying a gage from the lot to a NBS standard (thermal expansion determined by interferometry), the temperature effects of the gage material is subtracted from the apparent data leaving the expansion characteristics of the material being tested.

The method is applicable to metals and ceramics and is non-destructive.

14.0 Brazing Difficult-to-Join Materials

Personnel: J. L. Nelson, J. R. Palmieri

Sponsorship: NASA Contract NAS 12-569

Research Report:

To compensate for thermal expansion variation (i. e. maintain a tight fit) between a boron carbide ceramic inertial wheel shaft and a beryllium gimbal, an intermediate aluminum member is brazed to both difficult-to-join materials.

Successful results have been obtained using a eutectic brazing alloy of aluminum-12% silicon (m. p. 1077°F) and a commercially pure aluminum (1100) spacer (m. p. 1200°F). The work is done under vacuum with a diffused electron beam as a heat source and using thin titanium vapor deposition pretreatments on both the beryllium and boron carbide faying surfaces to promote wetting.

Metallographic examination of the joints requires special techniques (e. g. use of bonded diamond lapping plates) because of the extreme hardness differences of components at the interfaces. During the brazing cycle, the braze alloy lifts the titanium coating and forms an intimate bond with the boron carbide and beryllium, both of which otherwise are very difficult to wet.

This work was carried out using the facilities of the MIT Welding Laboratory.

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 primarily in the Solid State Division of the Laboratory.

Sponsorship

The Lincoln Laboratory is a center for research operated by Massachusetts Institute of Technology with the support of the U.S. Air Force under Contract AF 19(628)-5167.

LINCOLN LABORATORY
SOLID STATE DIVISION

Personnel:

Professor A. L. McWhorter, Division Head
Dr. P. E. Tannenwald, Associate Division Head
M. J. Hudson, Division Assistant
E. P. Warekois

Publications:

The work of the Solid State Division is reported in detail in the quarterly "Solid State Research Reports," Lincoln Laboratory, MIT (1968, Nos. 1, 2, 3 and 4) and in individual publications.

P. E. Tannenwald and R. Weber, "Comments on "Standing Spin-Wave Resonance in 'Flash-Evaporated' Permalloy Films," Phys. Rev. Letters 20, 918 (1968).

Theses:

- J. L. Sigel, "Studies in the Theory of the Transport Properties of an Interacting Electron Gas in the Presence of Random Impurities," Ph.D. Thesis, Physics Department, Harvard University, June 1968.
- M. S. Maltz, "A Magnetoreflexion Study of Arsenic and Bismuth," Ph.D. Thesis, Department of Electrical Engineering, MIT, June 1968.
- J. J. Stickler, "Spin Resonance in Spiral-Spin Structure Compounds," Sc.D. Thesis, Department of Metallurgy, MIT, July 1968.
- D. D. Buss, "Characterization of the Lattice Vibration Spectrum in PbTe," Ph.D. Thesis, Department of Electrical Engineering, MIT, August 1968.
- R. L. Carman, "Third Order Optical Non-Linearities and Propagation of Intense Light Beams," Ph.D. Thesis, Physics Department, Harvard University, September 1968.

RESEARCH REPORTS

1.0 Solid State Theory

Dr. H. J. Zeiger, Leader

Dr. M. M. Litvak, Assistant Leader

Staff Members:

Dr. P. N. Argyres

Dr. P. L. Kelley

Dr. G. F. Dresselhaus

Dr. W. H. Kleiner

Dr. D. C. Hamilton

Dr. D. M. Larsen

Dr. J. Hanus

Dr. J. L. Sigel

Dr. T. A. Kaplan

Dr. H. E. Stanley

Graduate Student Research Assistants:

S. R. Chinn, Electrical Engineering

Research Report:

A new generalization of Hartree-Fock (HF) theory to non-zero temperature, namely the Thermal Single-Determinant Approximation, has been applied (a) to a homogeneous interacting electron gas, with the result that a plane wave solution is found with identical thermodynamic behavior to that of the standard thermal HF approximation and (b) to H-atoms, where the new theory gives a lower free energy than the STHFA. Furthermore, the new theory requires that for weakly interacting atoms the one electron functions ψ_i be localized whereas the STHFA requires that the ψ_i be extended throughout the crystal.

Using a generalization of a method developed by P. Resibois for a pure interacting Fermi gas, the transport properties for weak and slowly varying disturbances have been investigated. Coefficients of the transport equation have been calculated for (a) a neutral or charged Fermi liquid in the presence of random impurities (b) dynamically independent fermions in the presence of dilute but arbitrarily strong impurity scattering centers and (c) a Fermi liquid in the generalized random phase approximation in the presence of dilute, but arbitrarily strong impurity scattering centers.

The high-temperature expansion method, applied to the Heisenberg model, has been used to investigate the dependence of the zero-field

susceptibility exponent on spin quantum number in ferromagnets and to compare the exponent of the staggered susceptibility of two- and three-dimensional antiferromagnets with other recent work.

Considering only nearest neighbor spin interactions, an exact solution for the energy, specific heat and susceptibility has been obtained for an open linear chain of arbitrary-dimensional spins and also for a Bethe lattice of coordination number z . A new general Hamiltonian with arbitrary ν -dimensional classical spins and also arbitrary lattice has been set up. This Hamiltonian reduces to the Ising, Vaks-Larkin, Heisenberg and spherical models, respectively for $\nu = 1, 2, 3$ and ∞ .

The Argyres-Kelley decoupling procedure for obtaining the reduced density matrix equations of motion for a system interacting with a bath and an external driving field has been used to find an expression for the contribution of a long wavelength spin wave to the susceptibility of a Heisenberg ferromagnet at low temperatures. The well-known spin wave renormalization and scattering terms are obtained, and in the low temperature limit, the susceptibility due to spin wave has the same form as that obtained using Green's function techniques.

Scattering of light from magnetic excitations in RbNiF_3 has been observed below T_c (139°K) and up to $\sim 200^\circ\text{K}$. From magnon assisted optical absorption and high temperature susceptibility data, exchange constants, are obtained which are consistent with the Raman scattering observations.

The effect of spin-density fluctuations on the scattering from single particle excitations in GaAs has been studied.

Because charge-density fluctuations are screened out in high electron concentration materials, while spin-density fluctuations are not, the spin-density fluctuations play an important role in this case. The polarization properties of the two mechanisms are also found to be different.

The influence of molecular interaction on the orientation of polarizable molecules in the presence of a strong ac orienting field has been studied. Under certain conditions, the molecular system can be driven into a new ordered phase, similar to a liquid crystal mesophase. The electric field intensity required for a certain induced change in the dielectric constant can be much smaller with the molecular interaction.

Publications:

- P. N. Argyres, "The Virial Theorem for a System of Interacting Particles Under External Forces and Constraints," Proc. Winter Institute in

- Quantum Chemistry, Solid-State Physics, and Quantum Biology, Sanibel Island, Int. J. Quan. Chem. I S, 699 (1967).
- S. R. Chinn and H. J. Zeiger, "Exchange Interactions and Raman Scattering from Spin Excitations in RbNiF_3 ," Phys. Rev. Letters 21, 1589 (1968).
- G. Dresselhaus and M. S. Dresselhaus, "An Effective Hamiltonian for the Optical Properties of Silicon and Germanium," Proc. Winter Institute in Quantum Chemistry, Solid-State Physics, and Quantum Biology, Sanibel Island, Int. J. Quan. Chem. I S, 595 (1967).
- J. Hanus, J. Feinleib and W. J. Scouler, "Band Structure of Nickel and Low-Energy Optical Transitions," J. Appl. Phys. 39, 1272 (1968).
- T. K. Gustafson, P. L. Kelley, R. Y. Chiao and R. G. Brewer, "Self-Trapping in Media with Saturation of the Nonlinear Index," Applied Phys. Letters 12, 165 (1968).
- D. M. Larsen, "Shallow Donors of InSb in a Magnetic Field," J. Phys. Chem. Solids 29, 271 (1968).
- D. M. Larsen, "Upper and Lower Bounds for the Intermediate Coupling Polaron Ground State Energy," Phys. Rev. 172, 967 (1968).
- M. M. Litvak, "Ultraviolet and Infrared Pumping of OH Molecules," Interstellar Ionized Hydrogen, edited by Yervant Terzian, (W. A. Benjamin, Inc., New York, 1968), p. 713.
- H. E. Stanley, "Dependence of Critical Properties on Dimensionality of Spins," Phys. Rev. Letters 20, 589 (1968).
- H. E. Stanley, "Critical Properties of Isotropically-Interacting Classical Spins Constrained to a Plane," Phys. Rev. Letters 20, 150 (1968).
- G. Dresselhaus and M. S. Dresselhaus, "Interpolation Methods for Phonon Spectra in Crystals," Int. J. Quan. Chem. (in press).
- J. Hanus, "Effect of the Molecular Interaction Between Anisotropic Molecules on the Optical Kerr Effect. Field-Induced Phase Transition," Phys. Rev. (in press).
- J. Hanus, "Influence of the Molecular Interaction on the AC Kerr Effect: Possibility of a Field-Induced Phase Transition," J. Quan. Elec. (in press).
- T. K. Gustafson, J-P. Taran, H. A. Haus, J. R. Lifstiz, and P. L. Kelley, "Self-Modulation, Self-Steepening and Spectral Development of Light in Small Scale Trapped Filaments," Phys. Rev. (in press).
- W. H. Kleiner and T. A. Kaplan, "Symmetry of the Ground Level of a Hamiltonian," J. Math. Phys. (in press).
- D. M. Larsen, "Intermediate Coupling Polaron Effective Mass," Phys. Rev. (in press).

- D. M. Larsen, "Effective Mass Theory for Polarons in External Fields," Phys. Rev. (in press).
- M. M. Litvak, "Infrared Pumping of Interstellar OH," Ap. J. (in press).
- J. L. Sigel, "A Transport Equation for Interacting Fermions in Random Scattering Centers," Phys. Rev. (in press).
- H. E. Stanley, "Spherical Model as the Limit of Infinite Spin Dimensionality," Phys. Rev. (in press).
- H. E. Stanley, "Exact Solution for a Linear Chain of Isotropically-Interacting Classical Spins of Arbitrary Dimensionality," Phys. Rev. (in press).

2.0 Electronic Materials

Dr. J. B. Goodenough, Leader

Dr. A. J. Strauss, Associate Leader

Staff Members:

Dr. R. J. Arnett	Mary C. Lavine (part time)
Dr. M. D. Banus	Dr. J. M. Longo
Dr. R. F. Brebrick, Jr.	J. R. O'Connor
A. Ferretti	E. B. Owens
Mary C. Finn	Dr. P. M. Raccach
Dr. G. W. Iseler	Dr. T. B. Reed
J. A. Kafalas	Dr. F. T. J. Smith
Dr. H. M. Kasper	Dr. J. M. Steininger

Graduate Student Research Assistants:

R. J. Temkin, Physics

Research Report:

Single crystals of a number of semiconductors and insulators have been grown by a variety of methods, including Bridgman (RbNiF_3 , CaF_2 , PbTe , $\text{CdTe}_{1-x}\text{Se}_x$ alloys), vertical zoning (Ag_3AsS_3), temperature gradient solution zoning (CdSe , $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ alloys), flux (EuO , $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ garnet, CdCr_2Se_4), open tube vapor transport (ZnSe , ZnS , CdS , Cd_3As_2), and closed tube vapor transport ($\text{ZnTe}_{1-x}\text{Se}_x$ alloys). A theoretical analysis of the forced convection (open tube) method of vapor growth, which is confirmed

by our data for iodine and camphor crystals, has shown that the growth velocity is proportional to the first power of the available concentration of condensing vapor and to the square root of the carrier gas velocity.

In order to investigate photoluminescence produced by isoelectronic traps in II-VI compounds, emission spectra due to oxygen in $\text{ZnTe}_{1-x}\text{Se}_x$, $\text{ZnTe}_{1-x}\text{S}_x$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ alloys and due to tellurium in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$, $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$, and $\text{ZnS}_{1-x}\text{Se}_x$ alloys have been measured at 4.2°K. As expected, the trapping energy is strongly affected by changes in the Group VI anion (e.g., in $\text{ZnTe}_{1-x}\text{Se}_x$ doped with oxygen) but not by changes in the Group II cation (e.g., in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ doped with tellurium). In the latter system, efficient photoluminescence is observed at room temperature over the whole range of compositions from ZnS to CdS.

Apparatus has been constructed for making resistivity and Hall coefficient measurements on compounds of volatile elements at temperatures up to about 1000°C under a controlled vapor pressure of one of the elements. This apparatus is being used to investigate deviations from stoichiometry as a function of temperature and pressure, ionization energies of lattice defects, and the temperature dependence of carrier mobilities. Measurements have been made on ZnTe and CdTe, and will be extended to other II-VI Compounds.

Several materials have been prepared and studied in a continuing program to substantiate the essential features of a three-component (T , n_f , b) phenomenological phase diagram for outer d electrons. For example, with one d electron per transition-metal atom per partially filled d band ($n_f = 1$), a T - b diagram contains a minimum of three critical b parameters: b_c , b_g , and b_{cs} , where b (which is proportional to the bandwidth) is the spin-independent, near-neighbor transfer energy of tight-binding theory. For $b < b_g$, electron correlations split a half-filled band in two, making it a semiconductor, and antiferromagnetic order is anticipated below a Neel temperature T_N . The maximum value of T_N occurs at $b_c < b_g$, where there is a change with increasing b from localized-electron antiferromagnetism to collective-electron antiferromagnetism.

For $b > b_g$, half-filled bands are not split in two by electron correlations, and the material is metallic, Pauli paramagnetic and, if $b > b_{cs} > b_g$, superconducting below a transition temperature T_{cs} . Examination of carefully characterized ingots of VO showed that $b \approx b_g$ in this material. The series of compounds YVO_3 , LaVO_3 ; PbCrO_3 , CaCrO_3 , SrCrO_3 ; CaMoO_3 , SrMoO_3 , BaMoO_3 , which are arranged in order of increasing b , demonstrate a b_c between LaVO_3 and PbCrO_3 , a b_g between CaCrO_3 and SrCrO_3 . The system $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ illustrates an antiferromagnetic to ferromagnetic

transition with increasing b in the plane $n_l = 4/3$; CoS_2 - CoSe_2 illustrates a ferromagnetic to antiferromagnetic transition with increasing b in the plane $n_l = 1/2$. Such changes have now been shown to illustrate important features of the phase diagram. The FeS_2 - CoS_2 - NiS_2 systems illustrate variations through the range $0 \leq n_l \leq 1/2$ with a simultaneous change from $b_c < b < b_g$ to $b > b_g$. Studies of the pressure variation of T_N or the Curie temperature T_C have also supported the essential features of the phase diagram.

Magnetic studies from 4.2 to 450°K in fields to 11k oe and under pressures to 14 kbar have been made in MnAs. A high-spin low-spin transition, shown by us to be due to a sharp reduction in the intra-atomic exchange splitting, was confirmed; and two metamagnetic states as well as a ferromagnetic state were identified in the high-pressure phase. A fundamental deficiency in the Bean-Rodbell model for the first-order phase change at T_C was pointed out.

A comprehensive summary, containing over 1700 references, of the crystallographic and magnetic properties of perovskites and perovskite-related compounds was submitted to Springer-Verlag for publication in the Landolt-Bornstein Tabellen. Motivated partly by this work and partly by the need for ferromagnetic materials that are transparent at optical frequencies, it was demonstrated that hydrostatic pressure converts compounds with the hexagonal CsNiCl_3 structure to the cubic-stacked structure of perovskite, CaTiO_3 , via three intermediary phases: the nine-layer structure of BaRuO_3 , the four-layer structure of SrMnO_3 , and the six-layer structure of ferrimagnetic RbNiF_3 (or of hexagonal BaTiO_3). The high-pressure phases are stable under ambient conditions; and from a knowledge of the stability of these phases as a function of pressure and ionic size, it has been possible to synthesize a number of new compounds, including several ferrimagnetic fluorides.

A number of garnets containing tellurium, with the type formula $\text{A}_3\text{Te}_2\text{B}_2\text{O}_{12}$, have been prepared by solid state reactions. They include the first garnets in which Co^{2+} ions occupy only tetrahedral sites, and a series in which A is a triply-charged rare earth ion and B is Li^+ . Another new series of rare earth compounds, with the type formula LnCrTeO_6 , has also been prepared. These have a structure similar to that of PbSb_2O_6 , but ordering of Cr and Te causes a doubling of the c -parameter.

The charge density of aluminum has been determined on an absolute scale by means of absolute intensity measurements of the first nine X-ray diffraction peaks obtained for a carefully prepared powder. For those peaks where the closed shell electrons make the major contribution, the measured scattering factors are in excellent agreement with the results of

relativistic Hartree-Fock atomic calculations, but disagree significantly with those of relativistic Hartree-Fock-Slater atomic calculations.

Publications:

- M. D. Banus, "Quenchable Effects of High Pressures and Temperatures on the Cubic Monoxide of Titanium", *Mat. Res. Bull.* 3, 723 (1968).
- R. F. Brebrick, "Tellurium Vapor Pressure and Optical Density at 370-615°C", *J. Phys. Chem.* 72, 1032 (1968).
- R. F. Brebrick, "Partial Pressure of $\text{Se}_2(\text{g})$ in Selenium Vapor", *J. Chem. Phys.* 48, 5741 (1968).
- R. F. Brebrick, "Si-Te System: Partial Pressures of Te_2 and SiTe and Thermodynamic Properties from Optical Density of the Vapor Phase," *J. Chem. Phys.* 49, 2584 (1968).
- J. B. Goodenough, "Localized vs Collective Descriptions of Magnetic Electrons", *J. Appl. Phys.* 39, 403 (1968).
- J. B. Goodenough, "Spin-Orbit-Coupling Effects in Transition-Metal Compounds", *Phys. Rev.* 171, 466 (1968).
- J. B. Goodenough, "Band Model for Transition-Metal Chalcogenides Having Layer Structures with Occupied Trigonal-Bipyramidal Sites", *Mat. Res. Bull.* 3, 409 (1968).
- J. B. Goodenough, J. M. Longo, and J. A. Kafalas, "Band Antiferromagnetism and the New Perovskite CaCrO_3 ", *Mat. Res. Bull.* 3, 471 (1968).
- J. M. Longo and A. W. Sleight, "Characterization and Structure of $\text{La}_4\text{Re}_6\text{O}_{19}$, A New Metal Cluster Compound", *Inorg. Chem.* 7, 108 (1968).
- J. M. Longo, P. M. Raccach, and J. B. Goodenough, "Magnetic Properties of SrRuO_3 and CaRuO_3 ", *J. Appl. Phys.* 39, 1327 (1968).
- J. M. Longo and J. A. Kafalas, "Pressure-Induced Structural Changes in the System $\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3$ ", *Mat. Res. Bull.* 3, 687 (1968).
- H. M. Kasper, "Preparation of $\{\text{A}_3^{2+}\}[\text{Te}_2](\text{B}_3^{2+})\text{O}_{12}$ -Garnets", *Mat. Res. Bull.* 3, 765 (1968).
- J. A. Kafalas and J. M. Longo, "Effect of Pressure on the Structure and Magnetic Properties of RbNiF_3 ", *Mat. Res. Bull.* 3, 501 (1968).
- P. M. Raccach and J. B. Goodenough, "A Localized-Electron to Collective-Electron Transition in the System $(\text{La}, \text{Sr})\text{CoO}_3$ ", *J. Appl. Phys.* 39, 1209 (1968).
- T. B. Reed and E. R. Pollard, "Tri-Arc Furnace of Czochralski Growth with a Cold Crucible", *J. Crystal Growth* 2, 243 (1968).

- J. M. Steininger and R. E. England, "Growth of Single Crystals of ZnTe and $\text{ZnTe}_{1-x}\text{Se}_x$ by Temperature Gradient Solution Zoning", Trans. Met. Soc. AIME 242, 444 (1968).
- J. M. Steininger, "Growth of CdSe Single Crystals by Temperature Gradient Solution Zoning in Excess Se", Mat. Res. Bull. 3, 595 (1968).
- A. J. Strauss, "Metallurgical and Electronic Properties of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$, and Other IV-VI Alloys", Trans. Met. Soc. AIME 242, 354 (1968).
- M. D. Banus and M. C. Lavine, "The P-T Diagram of InSb at High Temperatures and Pressures", J. Appl. Phys. (in press).
- R. F. Brebrick, "Homogeneity Ranges and Te_2 -Pressure Along the Three-Phase Curves for $\text{Bi}_2\text{Te}_3(\text{c})$ and a 55-58 at % Te, Peritectic Phase", J. Phys. Chem. Solids (in press).
- R. F. Brebrick, "Characterization of Phases in the 50-60 at % Te Region of the Bi-Te System by X-ray Powder Diffraction Patterns", J. Appl. Crystallography (in press).
- J. B. Goodenough, "Descriptions of Outer d Electrons in Thiospinels", J. Phys. Chem. Solids (in press).
- J. B. Goodenough and J. M. Longo, "Crystallographic and Magnetic Properties of Perovskite and Perovskite-related Compounds", Landolt-Bornstein Tabellen (in press).
- H. M. Kasper, " LnCrTeO_6 - A New Series of Compounds Based on the PbSb_2O_6 Structure", Mat. Res. Bull. (in press).
- T. B. Reed, W. J. LaFleur, and A. J. Strauss, "Diffusion and Convection in Vapor Crystal Growth", Proceedings of International Conference on Crystal Growth (in press).
- A. J. Strauss and R. F. Brebrick, "Deviations from Stoichiometry and Lattice Defects in IV-VI Compounds and Their Alloys. General Features and Experimental Methods", J. Physique (in press).

3.0 Solid State Physics

Dr. J. G. Mavroides, Leader

Dr. G. B. Wright, Assistant Leader

Staff Members:

Dr. F. A. Blum

Dr. R. C. Brandt

Dr. P. P. Crooker

Dr. E. J. Johnson

Dr. W. E. Krag

Dr. J. Melngailis

Dr. M. S. Dresselhaus (part time)	N. Menyuk
K. Dwight, Jr.	Dr. K. W. Nill
Dr. J. Feinleib	Dr. A. S. Pine
Dr. S. H. Groves	Dr. W. J. Scouler
Dr. V. E. Henrich	Dr. R. Weber

Graduate Student Research Assistants:

N. D. Strahm, Electrical Engineering
E. J. Tichovolsky, Physics
J. Waldman, Physics

Research Report

The Solid State Physics Group investigates primarily the behavior of electrons in solids. The research during the past year can be classified into three categories: (1) band structure, (2) magnetic interactions and ordering, and (3) scattering experiments with lasers.

3.1 Band Structure

The extra transitions in InSb observed by magnetoreflexion and magnetoelectroreflexion have been analyzed to yield values for the warping parameters and the linear - k splitting of the valence band. Also in InSb, combination spin and cyclotron resonance transitions have been observed, allowing a study through the reststrahl frequency region. The results indicate an unexpected polaron interaction of the electron-TO phonon.

Bismuth-antimony alloys, in the range of composition $0 < \% \text{ Sb} < 15$ have been investigated using the magnetoreflexion technique. The results have been analyzed in terms of the Lax two-band model to obtain the band parameters and their variation with composition. The Fermi surfaces of PbTe-SnTe alloys were studied by means of the Shubnikov-de Haas effect. Measurements were carried out on 17, 20 and 30% tin alloys with magnetic fields up to 80 kG (using the facilities of MIT's National Magnet Laboratory).

The optical investigation of the band structure of nickel has now been extended to nickel-copper alloys. Reflection measurements from 0.2 to 11 eV in several alloys seem to indicate that below 4 eV the alloys behave according to a "localized states" or to a "minimum polarity" model. An analysis of recent optical and transport data for NiO indicates a localized crystal-field type optical spectrum and also an itinerant band-like

nonactivated conductivity mobility. A procedure was suggested for portraying both these properties on a single diagram, analogously to the band structure diagram of simpler materials.

3.2 Magnetic Interactions and Ordering

Measurements of the magnetic phase diagram of MnAs under pressure, in the temperature range between 50° and 350°K, were extended to 11 kilobars. It was found that unless third-order strain effects are included, even a generalized form of the Bean-Rodbell thermodynamic theory is unable to explain the change in sign at the hexagonal-orthorhombic transition of the pressure dependence of the paramagnetic Curie temperature.

The investigation of microwave resonance spectra of insulating magnetic spiral structures was extended to ZnCr_2S_4 and ZnCr_2Se_4 . Theoretical models of the magnetic ordering were obtained.

In chromium spinels having non-magnetic A sites, it was shown that five distinct distant neighbor B-B exchange interactions can play significant roles in determining the ground state spin configurations. Extension of this work to CoCr_2O_4 , with magnetic A-site ions and A-A interactions, results in (a) an 8% decrease in the theoretical wavelength of the ferromagnetic spiral and (b) an additional magnetic transition at a temperature of about one third of T_c . These results bring theory in overall agreement with experiment.

3.3 Scattering Experiments with Lasers

Several experiments were carried out in α -quartz. The velocity and attenuation of 28 GHz hypersound was investigated by Brillouin scattering. Although the velocity variation with temperature in the range 300° to 600°K agrees with earlier measurements, the hypersonic attenuation agrees only in order of magnitude with the ultrasonic data. The temperature dependence of the damping of two optic vibrations, the 128 cm^{-1} E-mode and the 466 cm^{-1} A_1 -mode, and a longitudinal acoustic vibration along the x-axis were measured by high resolution Raman and Brillouin scattering. The residual damping of the 128 cm^{-1} mode at low temperatures was accounted satisfactorily by a simple model for the cubic anharmonicity.

Using an argon-ion laser and a surface reflection technique, Raman scattering from zone-center optic phonons has been studied in InSb and InAs from 5° to 300°K. In both these semiconductors an enhancement of the

LO phonon scattering intensity takes place when the laser frequency is near an interband transition; furthermore in InAs, an LO phonon scattering enhancement and also a decrease in the LO scattering frequency is obtained when the surface is biased with an electric field. The latter results can be explained in terms of the change in dielectric constant with surface electric field.

It has been suggested that the magneto-Raman scattering with $\Delta n = 1$, $\Delta s = 0$ which is observed in InSb might arise from two single electron mechanisms, namely interactions (a) due to the linear - k inversion asymmetry in the $\mathcal{E}(k)$ of the valence band and (b) between Landau levels which occur with $k_3 \neq 0$, where k_3 is along the magnetic field. A careful evaluation of these mechanisms gives a cross-section several orders of magnitude smaller than the experimental result, thus suggesting that other mechanisms, perhaps Coulomb interactions, are important.

An experimental and theoretical study of thermal self-defocusing arising from the propagation of a laser beam in an absorbing liquid has been completed. The transient approach to steady state and steady state effects were investigated. A similar study was made of thermal self-focusing in glass.

Publications:

- R. L. Carman and P. L. Kelley, "Time Dependence in Thermal Blooming of Laser Beams," *Appl. Phys. Letters* **12**, 241 (1968).
- D. H. Dickey and D. M. Larsen, "Evidence for Electron-to-Phonon Interaction in InSb," *Phys. Rev. Letters* **20**, 65 (1968).
- M. Maltz and M. S. Dresselhaus, "Observation of Interband Transitions in Arsenic," *Phys. Rev. Letters* **20**, 919 (1968).
- P. R. Schroeder, M. S. Dresselhaus and A. Javan, "Location of Electron and Hole Carriers in Graphite from Laser Magnetoreflexion Data," *Phys. Rev. Letters* **20**, 1292 (1968).
- K. Dwight and N. Menyuk, "Analysis of Distant-neighbor Interactions in Cubic Spinels," *J. Appl. Phys.* **39**, 660 (1968).
- J. Feinleib, W. J. Scouler and A. Ferretti, "Optical Properties of the Metal ReO_3 from 0.1 to 22 eV," *Phys. Rev.* **165**, 765 (1968).
- J. Feinleib and D. Adler, "Band Structure and Electrical Conductivity of NiO ," *Phys. Rev. Letters* **21**, 1010 (1968).
- G. H. Stauss, M. Rubinstein, J. Feinleib, K. Dwight, N. Menyuk, and A. Wold, "NMR and Magnetization Studies of CdCr_2Se_4 ," *J. Appl. Phys.* **39**, 667 (1968).

- C. R. Pidgeon and S. H. Groves, "Linear-k Valence Band Splitting in InSb," *Phys. Rev. Letters* 20, 1003 (1968).
- N. Menyuk, P. M. Raccach and K. Dwight, "Magnetic Properties of $\text{La}_{.5}\text{Sr}_{.5}\text{CoO}_3$ Near its Curie Temperature," *Phys. Rev.* 166, 510 (1968).
- N. Menyuk, "Nonmetals," *Magnetism and Magnetic Materials - 1968 Digest*, H. Chang and T. R. McGuire, eds., Academic Press, New York, (1968), p. 77.
- K. W. Nill, "Microwave Acoustic Amplification in n-InSb at 9 GHz," *Phys. Rev. Letters* 21, 82 (1968).
- J. J. Stickler and H. J. Zeiger, "Observation of Ferri- and Antiferromagnetic Resonance in Insulating Magnetic Spiral Structures," *J. Appl. Phys.* 39, 1021 (1968).
- R. Weber, "Magnon-Phonon Coupling in Metallic Films," *Phys. Rev.* 169, 451 (1968).
- R. Weber, "Magnetic Resonance," *Magnetism and Magnetic Materials - 1968 Digest*, H. Chang and T. R. McGuire, eds., Academic Press, (1968), p. 160.
- R. Weber, "Spin Wave Resonance," *IEEE Trans. on Magnetics*, Vol. Mag-4, No. 1 (1968).
- K. Dwight and N. Menyuk, "Distant-Neighbor B-B Interactions in Cobalt Chromite," *Proceedings of 14th Annual Conference on Magnetism and Magnetic Materials*, New York, 18-21 November 1968, *J. Appl. Phys.* (in press).
- J. Feinleib, W. J. Scouler and J. Hanus, "Optical Studies and Band Structure of Cu-Ni Alloys," *Proceedings of 14th Annual Conference on Magnetism and Magnetic Materials*, New York, 18-21 November 1968, *J. Appl. Phys.* (in press).
- J. Feinleib, "Band Approach to the Transition Metal Oxides," *Proceedings of International Advanced Summer Physics Institute*, Chania, Crete, Greece, 1-12 July 1968 (in press).
- D. Adler, and J. Feinleib, "Band Structure of Magnetic Semiconductors," *Proceedings of 14th Annual Conference on Magnetism and Magnetic Materials*, New York, 18-21 November 1968, *J. Appl. Phys.* (in press).
- S. H. Groves, C. R. Pidgeon, A. W. Ewald and R. J. Wagner, "Interband Magnetoreflexion of Gray Tin," *Proceedings of 9th International Conference on Physics of Semiconductors*, Moscow, USSR, 23-29 July 1968 (in press).
- C. R. Pidgeon and S. H. Groves, "Electroreflexion Study of Inversion

- Asymmetry and Warping Induced Interband Magneto-Optical Transitions in InSb," Proceedings of 9th International Conference on Physics of Semiconductors, Moscow, USSR, 23-29 July 1968 (in press).
- E. J. Johnson, "An Exciton in a High Magnetic Field - Germanium," Proceedings of 9th International Conference on Physics of Semiconductors, Moscow, USSR, 23-29 July 1968 (in press).
- J. G. Mavroides, "Magneto-Optical Properties," Optical Properties of Solids, F. Abeles, ed., North Holland Publishing Company (in press).
- N. Menyuk, J. A. Kafalas, K. Dwight and J. B. Goodenough, "Effect of Pressure on the Magnetic Properties of MnAs," Phys. Rev. (in press).
- N. Menyuk, J. A. Kafalas, K. Dwight and J. B. Goodenough, "Pressure Effect Measurements Using a Vibrating-coil Magnetometer," Proceedings of 14th Annual Conference on Magnetism and Magnetic Materials, New York, 18-21 November 1968, J. Appl. Phys. (in press).
- A. S. Pine, "Thermal Brillouin Scattering Study of the Attenuation of Hypersound in Quartz," Proceedings of International Conference on Light Scattering Spectra of Solids, New York University, 3-6 September 1968 (in press).
- A. S. Pine and P. E. Tannenwald, "Temperature Dependence of Raman Linewidth and Shift in α -Quartz," Phys. Rev. (in press).
- W. J. Scouler, "Optical Properties of Mg_2Si , Mg_2Ge and Mg_2Sn from 0.6 to 11.0 eV at 77°K," Phys. Rev. (in press).
- N. D. Strahm and A. L. McWhorter, "Raman Scattering from Lattice Vibrations of $\text{GaAs}_{1-x}\text{P}_x$," Proceedings of International Conference on Light Scattering Spectra of Solids, New York, 3-6 September 1968 (in press).
- G. B. Wright, P. L. Kelley and S. H. Groves, "Landau Level Raman Scattering," Proceedings of International Conference on Light Scattering Spectra of Solids, New York, 3-6 September 1968 (in press).
- G. B. Wright and A. Mooradian, "Electronic Raman Scattering from Impurities in Semiconductors," Proceedings of 9th International Conference on Physics of Semiconductors, Moscow, USSR, 23-29 July 1968 (in press).

4.0 Applied Physics

Dr. J. O. Dimmock, Leader
T. C. Harman, Assistant Leader
Dr. I. Melngailis, Assistant Leader

Staff Members:

Dr. J. F. Butler	Dr. W. T. Lindley
A. R. Calawa	Dr. A. Mooradian
T. F. Clough	Dr. R. J. Phelan, Jr.
Dr. J. P. Donnelly	Dr. G. E. Stillman
Dr. A. G. Foyt	Dr. C. M. Wolfe
Dr. C. E. Hurwitz	P. Youtz

Graduate Student Research Assistants:

S. Brueck, Electrical Engineering
 R. A. Murphy, Electrical Engineering
 M. R. Oliver, Electrical Engineering

Research Report:

Infrared radiation in the wavelength region between $200\ \mu$ and 2mm was modulated utilizing free carrier absorption by impact ionized electrons in germanium at 4.2°K . Modulation depths up to 100% and bandwidths of 100 MHz have been achieved for 2mm wavelength radiation. In a communications-type experiment, $337\ \mu$ cyanide laser radiation was modulated by applying an audio modulated 300 kHz carrier to the Ge crystal. The transmitted radiation was incident on a fast GaAs photoconductive detector which was connected to a radio receiver tuned to 300 kHz where the audio information was recovered.

Infrared transmission, magnetic birefringence and Faraday rotation have been measured in single crystals of EuO in the wavelength range between 1.5 and $20\ \mu$. The most transparent samples have an absorption coefficient at 20°K less than $0.5\ \text{cm}^{-1}$ in the range between 2.5 and $9\ \mu$ and less than $1.0\ \text{cm}^{-1}$ at $10.6\ \mu$. At 20°K and 9 kG the Faraday rotation varies from $660\ \text{deg/cm}$ at $10.6\ \mu$ to over $10^5\ \text{deg/cm}$ at $1.5\ \mu$. The figure of merit for the specific rotation per unit attenuation is $150\ \text{deg/dB}$ at $10.6\ \mu$ and $> 1.4 \times 10^4\ \text{deg/dB}$ at $2.5\ \mu$.

The combined effects of applied DC bias and short wavelength radiation on the properties of InSb-MOS infrared detectors have been investigated. Several processes have been isolated and identified. For photon energies greater than 0.7 eV, electrons are photoemitted from the InSb into the oxide where they may become trapped. For photon energies greater than between 1.0 to 3.0 eV, depending upon the initial charge state of the system,

the oxide layer becomes photoconductive. These effects are reflected in the response of the InSb-MOS detector to 3.9μ InSb diode radiation.

Extrinsic far infrared photoconductivity has been observed at 4.2°K in high purity n-type epitaxial layers of GaAs grown on Cr-doped semi-insulating GaAs substrates. Detectivities as high as $1.7 \times 10^{10} \text{ cm/Wsec}^{\frac{1}{2}}$ and $1.4 \times 10^{11} \text{ cm/Wsec}^{\frac{1}{2}}$ have been measured at 195 and 337μ , respectively. The time constant of the detector has been determined to be shorter than $1\mu\text{sec}$ using the Ge avalanche modulator to chop the incident radiation. A time constant of about 5 nsec was measured using impact impurity ionization in the GaAs.

Guard rings consisting of epitaxial n-GaAs have been grown for GaAs p-n junction and Schottky barrier avalanche diodes utilizing the $\text{AsCl}_3\text{-Ga-H}_2$ flow system. The breakdown voltage for the guarded structures is higher than for those without a guard ring, and in avalanche breakdown light is emitted nearly uniformly across the diode, whereas in unguarded diodes light emission is at the perimeter. The guarded diodes have been used as avalanche photodetectors and show a gain in excess of 100 when biased near reverse breakdown.

It has been found that proton radiation damage can be used to convert both p- and n-type GaAs into high resistivity material, and this technique has been used to isolate p-n junctions on a diffused GaAs substrate and also to prevent edge breakdown in Au-GaAs Schottky barriers.

Gallium-tin melts have been used in the $\text{AsCl}_3\text{-Ga-H}_2$ flow system to prepare n-type epitaxial GaAs with accurately controlled, uniform electron carrier densities in the range between 10^{15} and 10^{17} cm^{-3} . The transfer ratio of net tin donor concentration in the epitaxial layer to tin concentration in the gallium melt depends over a wide range of conditions primarily on only the growth rate of the epitaxial layer. Utilizing this property layers with doping variations as low as ± 2.6 percent have been obtained by growth under conditions where small variations in the system conditions have little effect on the growth rate.

High-resistivity surface layers up to 4μ deep have been produced in 4-ohm-cm p-type ZnTe by bombardment with approximately 10^{14} protons/ cm^2 from a 400 kV van de Graaff generator. Contact to contact resistance between ohmic contacts on the front surface increased from about 200 to greater than 10^9 ohms after bombardment.

Vapor grown single crystals of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with (100) surfaces 1 mm^2 or larger have been prepared in a special evacuated fused silica ampoule using a coarsely ground two-phased metal-rich ingot of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with a metal/Te ratio of 51/49 as the vapor source. The crystals are grown,

annealed and any junctions are formed in the closed ampoule by adjusting the temperature. From these crystals, diode lasers with low thresholds and emission wavelengths up to 28.1μ have been fabricated.

The properties of bismuth doped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ diode lasers have been examined for x in the range $0.24 \lesssim x \lesssim 0.27$, where it is difficult to obtain high carrier concentration n-type material by deviations from stoichiometry only. The main effect of doping with Bi is believed to be a shift in the composition at which $n = p$ to the Te-rich side of the stoichiometric line. This allows larger n-type carrier concentrations to be obtained with shorter annealing times. The Bi doping also reduces the laser threshold current densities at both 12° and 77°K . At 77°K undoped diodes in this composition range did not exhibit laser emission up to $30,000 \text{ A/cm}^2$ while doped diodes had threshold currents between 1000 and 5000 A/cm^2 .

Photoconductivity at wavelengths up to 15μ has been observed at 77°K in Bridgman-grown and subsequently annealed crystals of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ which had carrier concentrations as low as $2 \times 10^{15} \text{ cm}^{-3}$ and 77°K mobilities of about $3 \times 10^4 \text{ cm}^2/\text{Vsec}$. Detectivity values between 10^8 and $10^9 \text{ cm/Wsec}^{1/2}$ at 4.2°K were measured. Photoconductive lifetimes of about 10^{-8} sec and about 10^{-6} sec were obtained at the two respective temperatures.

The zero bias impedance of a number of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ diodes has been increased by as much as 10^3 through electrolytic etching. This result has contributed to the significantly improved performance of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ photo-voltaic detectors and lasers.

Photovoltaic detectors with long-wavelength cutoffs up to 20μ at 77°K and up to 30μ at 12°K have been produced from annealed Bridgman-grown and vapor-grown $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals in the $0 < x < 0.25$ composition range. Responsivities as high as 190 V/W , and external quantum efficiencies up to 37% have been obtained at wavelengths up to 12μ in diodes operated at 77°K .

A study of metal inclusions and low-angle grain boundaries in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ crystals has indicated that these defects are due to constitutional supercooling during growth. This explanation indicates that these defects may be avoided by growing from a sufficiently tellurium-rich melt, by growing in a steep temperature gradient or by decreasing the growth rate. Crystals grown from a $(\text{Pb}_{1-x}\text{Sn}_x)_0.49\text{Te}_{0.51}$ melt have been found to be essentially free of these macroscopic defects.

Publications:

J. F. Butler and T. C. Harman, "Long Wavelength Infrared $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ Diode Lasers," *Appl. Phys. Letters* 12, 347 (1968).

- A. R. Calawa, T. C. Harman, M. Finn and P. Youtz, "Crystal Growth, Annealing and Diffusion of Lead-Tin Chalcogenides," *Trans. Metallurgical Soc. AIME* 242, 374 (1968).
- J. M. Besson, A. R. Calawa, and W. Paul, "The Tuning of PbSe Lasers by Hydrostatic Pressure from 8 to 22 Microns," *Phys. Rev.* 173, 699 (1968).
- R. E. Watson, A. J. Freeman, and J. O. Dimmock, "Magnetic Ordering and the Electronic Properties of the Heavy Rare Earth Metals," *Phys. Rev.* 167, 497 (1968).
- J. P. Donnelly, A. G. Foyt, E. D. Hinkley, W. T. Lindley, and J. O. Dimmock, "Type Conversion and p-n Junctions in n-CdTe Produced by Ion Implantation," *Appl. Phys. Letters* 12, 303 (1968).
- I. Melngailis and P. E. Tannenwald, "Far Infrared Impact Ionization Modulators," *1968 NEREM Record*, p. 152 (November 1968).
- I. Melngailis and T. C. Harman, "Photoconductivity in Single-Crystal $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$," *Appl. Phys. Letters* 13, 180 (1968).
- A. Mooradian, "Light Scattering from Single-Particle Electron Excitations in Semiconductors," *Phys. Rev. Letters* 20, 1102 (1968).
- G. E. Stillman, C. M. Wolfe, I. Melngailis, C. D. Parker, P. E. Tannenwald, and J. O. Dimmock, "Far Infrared Photoconductivity in High Purity Epitaxial GaAs," *Appl. Phys. Letters* 13, 83 (1968).
- C. M. Wolfe, A. G. Foyt, and W. T. Lindley, "Epitaxial Gallium Arsenide for High-Efficiency Gunn Oscillators," *Electrochem. Technol.* 6, 208 (1968).
- J. F. Butler and T. C. Harman, "Metallic Inclusions and Cellular Substructure in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ Single Crystals," *J. Electrochem. Soc.* (in press).
- J. F. Butler and T. C. Harman, "Bismuth Doped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ Diode Lasers with Low Threshold Currents," *IEEE J. Quantum Electronics* (in press).
- J. O. Dimmock, C. E. Hurwitz, and T. B. Reed, "Infrared Transmission, Magnetic Birefringence and Faraday Rotation in EuO," *Appl. Phys. Letters* (in press).
- A. G. Foyt, W. T. Lindley, C. M. Wolfe, and J. P. Donnelly, "Isolation of Junction Devices in GaAs Using Proton Bombardment," *Solid State Electronics* (in press).
- I. Melngailis and T. C. Harman, "Single Crystal Lead-Tin Chalcogenides," book chapter, *Semiconductors and Semimetals*, Vol. VII (Academic Press) (in press).
- I. Melngailis, "Laser Action and Photodetection in Lead-Tin Chalcogenides,"

Proc. Intl. Colloq. on IV-VI Compounds, Paris, France, 1968
(Journal de Physique) (in press).

- A. Mooradian, "Light Scattering from Single-Particle Electron and Hole Excitations in Semiconductors," Proc. Intl. Conf. on Light Scattering Spectra of Solids (Springer-Verlag Publishers) (in press).
- A. Mooradian and A. L. Mc Whorter, "Light Scattering from Plasmons and Phonons in GaAs," Proc. Intl. Conf. on Light Scattering Spectra of Solids (Springer-Verlag Publishers) (in press).
- C. M. Wolfe and W. T. Lindley, "Epitaxially Grown Guard Rings for GaAs Diodes," J. Electrochem. Soc. (in press).
- C. M. Wolfe, G. E. Stillman, and W. T. Lindley, "Tin Doping of Epitaxial Gallium Arsenide," Proc. of Intl. Conf. on GaAs, Dallas, Texas, 1968 (Institute of Physics and the Physical Society) (in press).

5.0 Computer Components (Data Systems Division)

Dr. D. O. Smith, Leader

Staff Members:

Dr. M. S. Cohen	R. C. Johnston
Dr. R. W. Davies	C. T. Kirk, Jr.
Dr. K. J. Harte	G. P. Weiss
Dr. E. E. Huber, Jr.	

Research Report

5.1 Magnetic Films

Determining Micromagnetic Structures by Lorentz Microscopy

A theory has been developed for determining one-dimensional micromagnetic structures from their corresponding Lorentz electron micrographs. This "inversion" procedure takes into account wave-optical effects to first order in the magnetic phase shift but is exact in the classical limit. Unlike previous methods of analysis, no model need be assumed a priori for the micromagnetic configuration. The inversion takes the form of a convolution integral over the electron contrast, and is most conveniently carried out on a computer.

The theory has been verified by a computer simulation in which the

electron contrast for a domain wall of simple form was calculated exactly. The wall profile given by the theory was then compared to the original wall. The results were found to be in close agreement for a very wide range of experimental parameters.

The inversion theory was then applied to domain walls in Ni-Fe films. For films 100-500 Å thick, walls were found to have nearly linear central portions, with widths on the order of 1000 Å and varying inversely with film thickness, and long tails extending at least 5000 Å from the wall center. For films greater than 500 Å thick, inelastic electron scattering, which was taken into account for the thinner films, became so large that no meaningful or self-consistent results could be obtained. An energy-selecting microscope to filter out the inelastic background appears to be necessary for such thick films.

The theory has also been applied to magnetization ripple in Ni-Fe films. The ripple traces obtained show, as expected, random fluctuations with "wavelengths" from about 1000 to 10,000 Å. Further studies involve Fourier analysis of these traces by means of a fast Fourier transform.

A complementary approach to the ripple problem is the use of an optical Fourier transform method in which the Lorentz micrograph becomes a diffracting object, or a hologram. The reconstructed image is then simply related to the two-dimensional Fourier transform of the ripple. This method has been successfully implemented by means of an argon laser with an interference cavity for stability and coherence.

5.2 Materials for Memory Applications

Magnetic-film memory systems have been proposed which are accessed by the simultaneous use of photon and electron beams [D. O. Smith, IEEE Trans. Magnetics MAG-3, 593 (1967)]. Such a memory uses the electron beam to write information by heating above the Curie point and subsequently cooling in a magnetic field. Reading is accomplished by illuminating the entire memory with light and thermally modulating the magneto-optical properties of a single selected bit. The original proposal was deficient in that no provision was made to reduce the photon shot noise from unselected bits to an acceptable level. One method of eliminating the background light from unselected bits is to take advantage of the fact that the diameter of a bit is of the order of the wavelength of light and hence the photon information signal will be diffracted out of the background beam. In order to prevent unselected bits from also acting as diffraction centers, the memory film is to be made of a rare-earth iron garnet. Now

consider three appropriate levels from the narrow-line rare-earth spectra, and choose the interrogating light to correspond to the energy difference between the top two levels. Furthermore the intermediate level is chosen to be thermally accessible from the ground state. Then with practical and proper choices for the storage temperature for the entire memory and for the electron beam induced heating for the selected bit, the ratio of diffracted light from an unselected to a selected bit can be made $> 10^{-7}$.

5.3 Hot Electron Transport in Metals

a. Theoretical

We have studied the relaxation of a hot electron distribution using a time-dependent Boltzmann equation approximation. Assuming the distribution function to be isotropic in momentum space at all times, the Boltzmann equation is integrated to give the time development of a sharply peaked initial distribution. In this fashion, one can study the shape of the distribution function as it relaxes. In addition, it is found that the rate of energy loss of a hot electron distribution depends sensitively on the shape of the distribution through high moments of the probability amplitude.

b. Experimental

The measurement of tunnel triodes by a small ac signal r parameter technique is shown to give a new way of directly measuring the oxide barrier height and barrier asymmetry. This type of measurement permits distinguishing between true hot electron collection and leakage currents. A saturation of the hot electron transport coefficient has been found vs the emitter-base bias. The most direct explanation for this saturation is that those hot electrons which are collected are mainly ballistic, i. e. that they have come from the emitter with little or no momentum change due to collisions. The Al base attenuation length has been measured to be 150 Å at 77°K for electrons 2.0 eV above the Fermi level. Collector voltage dependence of the triode has been explained on the basis of electron-phonon losses in the collector oxide. The major part of the large hot electron attenuation factor in these triodes cannot be explained by either metal base losses or electron-phonon losses in the oxides, which together give rise to an attenuation factor of $\approx (1/100)$ remaining after taking the above volume losses into account.

Publications:

- C. T. Kirk, Jr. and E. E. Huber, Jr., "The Oxidation of Aluminum Films in Low-Pressure Oxygen Atmospheres," *Surface Science* 9, 217 (January 1968).
- D. O. Smith, "Proposal for a Magnetic-Film Memory Accessed by Combined Photon and Electron Beams," *IEEE Trans. Magnetics* MAG-3, No. 4, 593 (December 1967).
- K. J. Harte, D. O. Smith, R. M. Anderson and R. C. Johnston, "Excitation of Uniaxial-Anisotropy Relaxation Processes in Magnetic Films by a Rotating Magnetic Anneal," *J. Appl. Phys.* 39, No. 2, Part I, 749 (February 1968).
- M. S. Cohen, "High Resolution Lorentz Microscopy," *J. Appl. Phys.* 39, No. 2, Part II, 1149 (February 1968).
- K. J. Harte, "Theory of Magnetization Ripple in Ferromagnetic Films," *J. Appl. Phys.* 39, No. 3, 1503 (February 1968).
- D. O. Smith, "New Methods of Magneto-Optical Signal Modulation and Detection," *J. Appl. Phys.* 39, No. 2, Part I, 570 (February 1968).
- M. S. Cohen, "Recent Developments in Lorentz Electron Microscopy," *IEEE Trans. Magnetics*, MAG-4, No. 1, 48 (March 1968).
- D. O. Smith, "Biography of the Third ICMF," *IEEE Trans. Magnetics*, MAG-4, No. 4, 3 (March 1968).
- K. J. Harte, D. O. Smith and M. Gross, "Anisotropy Annealing by Diffusion of Interacting Defects Between Grain Boundaries in Magnetic Films," *Colloquium on Physics of Magnetic Thin Films at Irkutsk, USSR* (July 1968).
- R. W. Davies, "Surface Potential of a Free Electron Metal in the RPA," *Surface Science* 11, 419 (1968).
- E. E. Huber, Jr., F. L. Johnston, Jr., and C. T. Kirk, Jr., "Hot Electron Transport in Al-Al₂O₃ Triodes Produced by Plasma Oxidation," *J. Appl. Phys.* 39, 5104 (October 1968).
- D. O. Smith, "Methods for Improving the Signal-to-Noise Ratio of Photon and Electron Beam Accessed Magnetic-Film Memory Systems," *IEEE Trans. Magnetics* (in press).
- M. S. Cohen, "Introduction" of "Thin Films" a chapter in *Magnetism and Magnetic Materials 1968 Digest* (Academic Press, New York and London, 1968) (in press).
- D. O. Smith, "Uniaxial Anisotropy" in "Thin Films" a chapter in *Magnetism and Magnetic Materials 1968 Digest* (Academic Press, New York and London, 1968) (in press).

- K. J. Harte, "Magnetization Ripple," in "Thin Films" a chapter in Magnetism and Magnetic Materials 1968 Digest (Academic Press, New York and London, 1968) (in press).
- M. S. Cohen, "Feasibility of Lorentz Readout of a High-Density Fast Magnetic Memory," IEEE Trans. Magnetics (in press).
- K. J. Harte and M. S. Cohen, "Determination of Domain Wall Profiles in Magnetic Films," J. Appl. Phys. (in press).

INDEX - FACULTY

383

D. Adler, Asst. Prof., Elec. Eng.	73
R. B. Adler, Prof., Elec. Eng.	82
A. S. Argon, Prof., Mech. Eng.	249, 252, 254
F. O. Arntz, Asst. Prof., Elec. Eng.	82
B. L. Averbach, Prof., Metal.	133
S. Backer, Prof., Mech. Eng.	261
R. F. Baddour, Prof., Chem. Eng.	298, 299
G. B. Benedek, Prof., Physics	21
C. A. Berg, Assoc. Prof. Mech. Eng.	249, 257
M. B. Bever, Prof., Metal.	161
J. F. Breedis, Asst. Prof. Metal	154
R. Brewer, Visiting Prof. Physics	61
D. D. Buss, Asst. Prof. Elec. Eng.	82
J. W. Cahn, Prof., Metal.	167
L. L. Chang, Assoc. Prof. Elec. Eng.	82
R. L. Coble, Assoc. Prof., Metal.	213
M. Cohen, Prof. Metal.	154
E. G. Cravalho, Asst. Prof., Mech. Eng.	293
C. K. Crawford, Asst. Prof. Elec. Eng.	129
P. L. deBruyn, Prof., Metal.	185
P. D. DeCicco, Asst. Prof., Physics	1
M. C. Deibert, Asst. Prof., Chem. Eng.	298
C. S. Draper, Prof. Aero and Astro; Director, Instrumentation Lab.	248
M. S. Dresselhaus, Prof. Elec. Eng.	73
J. F. Elliott, Prof., Metal.	180
D. J. Epstein, Prof., Elec. Eng.	105
M. Feld, Asst. Prof. Physics	61
M. C. Flemings, Assoc. Prof. Metal.	188
C. W. Garland, Assoc. Prof., Chemistry	33
H. C. Gatos, Prof., Metal.	197
J. Gerstmann, Asst. Prof., Mech. Eng.	293
E. S. Gifillan, Visiting Prof., Mech. Eng.	261
E. R. Gilliland, Prof., Chem. Eng.	301, 310
N. J. Grant, Prof., Metal.	172
P. E. Gray, Prof., Elec. Eng.	82
T. J. Greytak, Asst. Prof., Physics	30
L. W. Gruenberg, Asst. Prof., Elec. Eng.	80, 207
A. S. Hoffman, Assoc. Prof., Chem. Eng.	297, 303, 310
A. Javan, Prof., Physics	61
K. H. Johnson, Asst. Prof., Metal.	133

R. C. Jones, Assoc. Prof., Civil Eng.	267
R. Kaplow, Assoc. Prof., Metal.	133
T. B. King, Prof., Metal.	180
W. D. Kingery, Prof., Metal.	213
D. Kleppner, Prof., Physics	12
G. Koppelman, Visiting Assoc. Prof., Physics	61
G. F. Koster, Prof., Physics	1
R. L. Kyhl, Prof., Elec. Eng.	56
B. Lax, Prof., Physics; Director, National Magnet Lab.	312
J. D. Litster, Asst. Prof., Physics	27
R. C. Lord, Prof., Chemistry	45
F. A. McClintock, Prof., Mech. Eng.	249
F. J. McGarry, Prof., Civil Eng.	267
A. L. McWhorter, Prof., Elec. Eng.; Division Head, Lincoln Lab.	360
J. W. Mar, Prof., Aero and Astro	259
E. A. Mason, Prof., Nuclear Eng.	307
E. W. Merrill, Prof., Chem. Eng.	301
F. Moavenzadeh, Assoc. Prof., Civil Eng.	267
M. Modell, Asst. Prof., Chem. Eng.	297, 299
C. J. Mogab, Asst. Prof., Metal.	213
J. S. Moore, Asst. Prof., Elec. Eng.	82
F. R. Morgenthaler, Prof., Elec. Eng.	105
S. C. Moss, Assoc. Prof., Metal.	133
R. Nevald, Visiting Asst. Prof., Elec. Eng.	82
R. E. Ogilvie, Prof., Metal.	241
C. H. Perry, Asst. Prof., Physics	49
G. W. Pratt, Prof. Elec. Eng.	73
E. Rabinowitz, Prof., Mech. Eng.	284
R. H. Rediker, Prof., Elec. Eng.	82
R. C. Reid, Prof., Chem. Eng.	303
B. G. Rightmire, Prof., Mech. Eng.	284
R. M. Rose, Assoc. Prof., Metal.	207
B. H. Rosof, Asst. Prof., Metal.	180
K. C. Russell, Asst. Prof., Metal.	167
C. N. Satterfield, Prof., Chem. Eng.	304
M. O. Scully, Asst. Prof., Physics	5
D. J. Sellmyer, Asst. Prof., Metal.	133
S. D. Senturia, Asst. Prof., Elec. Eng.	82
D. P. Shoemaker, Prof., Chem.	40
C. G. Shull, Prof., Physics	15

R. J. Silbey, Asst. Prof., Chem.	43
J. C. Slater, Institute Prof. Emeritus, Physics	1
A. Smakula, Prof., Elec. Eng.	112
A. C. Smith, Assoc. Prof., Elec. Eng.	82
J. L. Smith, Jr., Assoc. Prof., Mech. Eng.	293
K. A. Smith, Asst. Prof., Chem. Eng.	301
D. L. Smythe, Asst. Prof., Elec. Eng.	82
R. E. Stickney, Assoc. Prof., Mech. Eng.	288
M. W. P. Strandberg, Prof., Physics	56, 303
W. D. Syniuta, Asst. Prof., Mech. Eng.	284
A. Szoke, Assoc. Prof., Physics	61
R. D. Thornton, Assoc. Prof., Elec. Eng.	82
H. H. Uhlig, Prof., Metal.	194
D. R. Uhlmann, Asst. Prof., Metal.	213, 238
J. N. Walpole, Asst. Prof., Elec. Eng.	82
B. D. Wedlock, Assoc. Prof., Elec. Eng.	82
R. B. Williamson, Asst. Prof., Civil Eng.	267
A. F. Witt, Assoc. Prof., Metal.	197
B. J. Wuensch, Asst. Prof., Metal.	213
J. Wulff, Prof., Metal.	207, 259
I. V. Yannas, Asst. Prof., Mech. Eng.	261
T. O. Ziebold, Assoc. Prof., Nuclear Materials, Nuclear Eng.	244
H. J. Zimmermann, Professor, Elec. Eng., Director of the Research Laboratory of Electronics	v

(continued from inside front cover)

National Institutes of Health

DE-105 (Ogilvie); DE-02384-03 (Cahn); HE-08598 (Merrill, K. A. Smith, Gilliland); 1-RO1-AM-11919-01 (Yannas); 1-RO1-AP-00859-0151 (Ogilvie); 1-RO1-GM-15310-02-BBCB (Lord).

Department of Commerce:

C-85-65 Northeast Corridor Transportation Project (Thornton, Navon, McGarry, Williamson, Moavenzadeh).

National Bureau of Standards:

CST-280 (Elliott); CST-164 (Backer).

Department of Interior, Office of Saline Water:

14-01-0001-1133 (Uhlig); 14-01-0001-1256 (Hoffman, Modell).

Department of Health, Education and Welfare:

PHS 1R01 DE 02769-01-DEN (deBruyn).

U. S. Public Health Service:

PH43-66-491 (Merrill, K. A. Smith, Gilliland).

Reproduction in whole or in part is permitted for any purpose of the United States Government.