ANNUAL TECHNICAL REPORT 1966-1967

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CENTER FOR MATERIALS SCIENCE AND ENGINEERING

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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from
Center for Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

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Table of Contents

FOREWORD

We are once again submitting an Annual Technical Report to ARPA on the work performed under Contract SD-90. This report will have a very limited circulation, namely, to ARPA and to the other ARPA supported Interdisciplinary Laboratories together with a few other laboratories with which we have close association. As usual, MIT will also issue an Annual Report entitled "Research in Materials Science and Engineering at MIT." The latter report normally appears in mid-April and is a rather bulky document which aims at reporting on the large number of research activities at the Institute which can reasonably be classed under Materials Science and Engineering. The research described in the present report will be included and would account for approximately 25 per cent of the total effort in this area. Although the ARPA supported work can, in fact, be readily identified in the large report, it is not easy in this way to get an overall view of the ARPA program. These smaller reports, of which this will be the third that we have issued, have been well received and we have felt it worth our while to continue with them.

The problem of deciding what material to include in this report is not an easy one. One might, for example, include only research which is supported by financial aid from ARPA, either in the form of salary support or equipment grants to individual professors. This in our opinion, however, would not give an adequate view of the total ARPA program because of the close interaction between programs financed by ARPA funds and other programs under the same professor, some of which make substantial use of capital equipment provided through our Central Facilities. We have once again decided to ask each professor who has salary support, either for himself, staff, or students, to submit a research report covering the whole of his activities in the materials field but indicating which items and staff are ARPA supported and also the origin of support for his other work. We hope in this way to give a better view of the whole program. In order to indicate which faculty, staff and students receive full salary support (even for part of an academic year) we have marked these by **; those who have partial support are marked *. Those unmarked have no salary support from ARPA although the majority make use of equipment and central facilities provided by ARPA.

In each case where support comes from federal government sources other than ARPA we have endeavored clearly to indicate the supporting agency. There is also a certain amount of support from MIT sources in the form of equipment grants, from funds made available by various foundations and also in the form of fellowships such as those given by the National Science Foundation. The numbers of graduate students receiving such grants should be clear from the staff lists but it has not been possible to include the various equipment grants in this report.

We have now completed our second year in the new Interdisciplinary Laboratory and the various research groups have settled down into a fairly distinct pattern. There have, of course, been changes. Some groups have disappeared through faculty transfers, and some new groups have been established. The Central Facilities are also now in full operation including four separate groups for the preparation of materials, namely, single crystals of insulating and optical materials, semiconductor single crystals, extremely pure metal single crystals and alloys of controlled composition, and ceramic-type materials. Various facilities are also available for the preparation of specimens from these materials including cutting, polishing, and orientation. Examination by means of chemical analysis, X-rays, electron diffraction and electron microprobe are also available. The most recent central facility to be established is that provided by a scanning electron microscope (Stereoscan). These facilities are described in more detail in the body of the report.

The most recently established new research group in the Interdisciplinary Laboratory is a small one from the Department of Chemical Engineering working on surface catalysis, particularly involving studies of semiconductor surfaces as catalysts. This group does not, in fact, have financial support from ARPA but is a good example of the interaction between disciplines. The main object of establishing the group in the Interdisciplinary Laboratory is so that it can interact with the semiconductor physicists and also make use of the low-energy electron diffraction equipment that is part of our Central Facilities. A new group established with ARPA support but not having space in the laboratory is that under Professor R. B. Williamson working in association with Professor F. J. McGarry of the Department of Civil Engineering and studying the basic

morphology of precipitates in cementitious materials. This is something of a new departure from our previous lines of research but offers an opportunity of applying basic techniques to a problem of very considerable practical importance.

A perusal of the research reports will show that a number of important advances have been made in the course of the past year. It is perhaps invidious to pick out from these advances any for special mention. However, we feel that the developments in the study of crystal growth by Professors Gatos and Witt and their students represent a real breakthrough in technique. We mentioned in last year's report their work on "striations" in crystals. Their technique of artificially introducing striations to produce the analogue of "growth rings" in crystals has proved to be a very powerful and fruitful one. By applying external stimuli, either in the form of generated low-frequency pressure waves or of Peltier heating by means of a low-frequency current, a timing mechanism is introduced into the crystal. By measuring the distance between the introduced striations which can be observed with sophisticated optical microscope techniques, the growth rate at any point can be immediately determined. Such fascinating phenomena as the growth of a crystal along a twin boundary have been observed and many other interesting effects associated with crystal growth.

Two new research groups in modern optics have been established; the first under Professor J. D. Litster is concerned with the use of optical methods for studying magnetism in transparent media, and the second under Professor T. J. Greytak is studying the scattering of light from liquid helium and from gases due to thermally excited fluctuations.

A class of materials which at one time was very fashionable both as a vehicle for the study of the basic properties of compound semiconductors and for applications as detector elements consists of the lead salt compounds PbS, PbSe, PbTe. As we mentioned in last year's report, some excellent theoretical work has been carried out on these salts and now a new program for the preparation of these materials is being undertaken by Professor R. H. Rediker and his group with a view to their further use as electronic devices. There are still some very difficult unsolved problems in the preparation of high-purity single crystals of

these substances mainly concerned with the control of deviations from stoichiometry. Some new approaches to the problem are being made and look very promising.

An interesting new development is the application of light scattering by Professor G. B. Benedek and his group to the study of large molecules of biological interest. This promises to be a very fruitful line of research and likely to lead to some new interdisciplinary programs, between those interested in biology, medicine, and physics.

We have again had a most encouraging year of interdisciplinary colloquia. A list of the talks given in the colloquium series is included in the report and it will be seen that they cover a wide variety of subjects presented both by visiting speakers and by faculty, staff and students of the Institute. A number of our faculty and staff members have again presented papers at international meetings and meetings of the professional societies and have visited a number of other laboratories to give talks, including other IDL's.

We feel that the main objects of the IDL program are being achieved including an increasing number of high quality students both at undergraduate and graduate level being interested in working on problems of materials science and engineering. Our Central Facilities are in great demand and are making a significant contribution to the research program in this important area of activity. We are glad, too, that we have been able to start a small number of new research programs and are encouraging exchange of ideas between the various disciplines. While the present financial climate is certainly giving us difficulties, especially when we come to make new plans, we are striving hard to maintain the level of activity which has been established, particularly in the training of graduate students.

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

17th November 1967

Materials Center Colloquia 1966-67

During the year a series of colloquia have been held, sponsored by the Materials Center. A list of titles and speakers will show the wide range of subjects covered.

Professor D. H. Rank
Head of the Department of Physics
The Pennsylvania State University
Brillouin Spectra, Spontaneous and Stimulated

Professor George W. Pratt
Department of Electrical Engineering, MIT
Pressure and Ultrasonic Effects
in Semiconductor Lasers

Professor August F. Witt
Department of Metallurgy, MIT
Impurity Heterogeneities in
Semiconductor Single Crystals

Dr. S. D. Senturia
Department of Electrical Engineering, MIT
Nuclear Resonance in Ferromagnetic
Chromium Tribromide

Dr. L. J. Neuringer
National Magnet Laboratory, MIT
Magnetoacoustic Attenuation in
High-Field Superconductors

Dr. Bernard Borie
Metals and Ceramics Division
Oak Ridge National Laboratory
Interpretation of Diffuse X-ray Intensity
Distributions from Disordered Alloys

Professor R. H. Rediker
Department of Electrical Engineering, MIT
Heterojunction Research and Semiconductor
Laser Research at Lincoln Laboratory

Dr. Gabor Kemeny
Ledgemont Laboratory
Kennecott Copper Corporation
The Monovalent Insulator - Metal Transition

Dr. Gene F. Dresselhaus
Lincoln Laboratory
An Effective Hamiltonian for the Optical
Properties of Silicon and Germanium

Professor Raymond F. Baddour
Department of Chemical Engineering, MIT
Semiconductor Catalysis

Professor L. M. Falicov
Institute for the Study of Metals
The University of Chicago
de Haas-van Alphen Effect
and Magnet Breakdown

Dr. C. B. Walker
Army Materials Research Agency
Watertown Arsenal
Lattice Vibrations in Phonon Dispersion
Relations in Molybdenum

Professor Douglas J. Scalapino
Department of Physics
University of Pennsylvania
Recent Work on Josephson Junctions

Dr. David G. Thomas
Bell Telephone Laboratories
Radiative and Non-Radiative
Recombination in Semiconductors

Dr. Peter J. Melz
Division of Engineering and Applied Physics
Harvard University
High Pressure Experiments on the Band
Structure of Metals and Semiconductors

Dr. Mildred S. Dresselhaus
Lincoln Laboratory
Magneto-optical Studies of the Energy
Band Structure of Semimetals

Dr. Alan J. Strauss
Lincoln Laboratory
Inversion of Conduction and Valence
Bands in $Pb_{1-x}Sn_xSe$ Alloys

Professor B. W. Batterman
Department of Materials Science and Engineering
Cornell University
Low Temperature Structural Transformations in
in the High Field Superconductors Nb_3Sn and V_3Si

Professor Russel C. Jones
Department of Civil Engineering, MIT
Deformation of Wire Reinforced
Metal Matrix Composites

Dr. Thomas J. Greytak
Department of Physics, MIT
Brillouin Scattering in Gases
as a Test of Kinetic Theories

Professor Rustum Roy, Director
Materials Research Laboratory
The Pennsylvania State University
Kinetic Explanations for Major Inconsistencies in
Current High Pressure Research: The Systems
Ge, CdS, SiO_2, S

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CENTRAL FACILITIES

The central facilities in the Interdisciplinary Laboratory are now well established and are providing an important unifying force as well as making important contributions to the research and training program. We have followed the deliberate policy of whenever possible building around an experienced faculty member who is pursuing an active research program in the particular field. In this way the capabilities of the central facilities are being maintained at the forefront of the art.

Central Machine Shop - Room 13-1028

P. Kelleher, Foreman, Ext. 6842
E. Newman, Machinist
E. Shmid, Machinist
E. Gempka, Machinist
T. Farrell, Shop Helper
F. Payne, Machinist (Student/Faculty Shop, 13-2045)
C. Desjardin, Machinist

This is a fully equipped general machine shop for general or high precision machining of metals, plastics or ceramics.

There are three milling machines for surfacing, cutting slots, grooves, etc. Two are equipped with optical scales for precise hole boring. All have rotary tables and dividing heads for angular indexing. There is also one horizontal milling machine.

A geared head drill will drill a 1" diameter hole in the center of a 24" circle and will fly cut an 8" diameter in a plate. For cutting plate, there is a metal cutting bandsaw with a 24" throat. Grindable metals can be surfaced on a 6" x 18" surface grinder.

There are four tool-room type lathes that are capable of high precision turning, boring, drilling and thread cutting, including metric pitches. There are also two larger lathes with a turning capacity of 16-1/2".

Ceramic Materials Processing Laboratory - Room 4-010

W. D. Kingery, Professor, Metallurgy
R. L. Coble, Associate Professor, Metallurgy
D. R. Uhlmann, Assistant Professor, Metallurgy
F. D. Wilson, Technician, Metallurgy, Ext. 2484

The Ceramic Materials Processing Laboratory is now in its fourth year of operation and is located in Room 4-010.

Additional equipment purchased this year includes a Covel surface grinder with automatic hydraulic feed. This is necessary for grinding the surfaces of hard materials to a high precision.

The processing facility has been a useful one in permitting design flexibility for both students and staff. Significant success has been achieved in making the facility responsive to the needs of the Center, and further progress in anticipated for the year to come.

Electronic Repair and Construction Service - Room 13-1028

E. L. Greenwood, Project Technician, Ext. 2113

The Electronic Repair and Construction Shop is engaged in the design, construction and testing of new electronic equipment and the repair of many types of electronic equipment and instruments. A valuable service of the facility is consultation with faculty, students and other technicians on their electronic problems.

Electronic Instrument Loan Service - Room 13-1025

E. L. Greenwood, Project Technician, Ext. 2113

The Instrument Loan Service is closely related to the Electronics Shop and functions under the supervision of the same technician. Instruments of general laboratory utility are periodically added for loan service when short-term needs are encountered.

Central Analytical Laboratory - Room 13-4139

D. L. Guernsey, DSR Staff, Ext. 3306
W. T. Martin, DSR Staff
L. A. Carrara, DSR Staff
W. W. Correia, Technical Assistant
R. Teitelbaum, Laboratory Assistant

The Central Analytical Laboratory is maintained as a service facility in support of research throughout MIT. Approximately 70 projects from many departments have made use of this service during the past year. It is equipped to perform complete chemical analysis for major and trace constituents of a wide range of inorganic materials.

Standard wet chemical analysis equipment is supplemented with a Sargent Automatic Titrator for repetitive titrations, a Leco induction heated unit and tube furnace for combustion carbon and sulfur determinations and a Conductrometric Carbon Analyzer for low amounts of carbon.

Analyses of gases are made with a Kjeldahl Digestion and Distillation apparatus for nitrogen, a Leco Oxygen Analyzer with gas chromatograph, a Leco Hydrogen Analyzer designed for hot extraction in vacuum, and a Fisher Gas Chromatograph for analysis of furnace atmospheres.

Trace analyses are made with a Beckman Spectrophotometer with Flame Photometer attachment, a Turner Photofluorometer, a Sargent Polarograph with microrange extender, a Fisher Controlled Potential Electroanalyzer and a Jarrell-Ash 3.4 meter Ebert Spectrograph with recording microphotometer.

Cooperative arrangements make available the facilities of the Lincoln Laboratory Analytical Section and the Department of Chemistry's Microchemical Laboratory. Arrangements can also be made with the Reactor group for neutron activation analysis, with the Electron Optics group for x-ray fluorescence analysis and with the Ceramics group for Differential Thermal Analysis.

Insulating and Optical Crystal Growth Facility - Room 13-3146

A. Smakula, Professor, Electrical Engineering, Ext. 3696
Dr. A. Linz, Research Associate, Electrical Engineering, Ext. 3208
Dipl. Ing. J. Kalnajs, DSR Staff, Ext. 2112
V. Belruss, DSR Staff, Ext. 2192
Dr. R. Mykolajewycz, DSR Staff, Ext. 6878
E. Farrell, DSR Staff, Ext. 3692
Dr. D. Gabbe, DSR Staff, Ext. 3698
K. Bangerskis, Technical Assistant, Ext. 6879
A. Vetrovs, Technical Assistant, Ext. 3692
R. Mills, Technician, Ext. 3697

The facility is equipped to handle three phases of crystal growth and evaluation.

1. Chemical preparation of feed materials of halide, fluoride, and oxides of various types can be accomplished. There are furnaces for calcining oxides in air and various gases, calcination of fluorides under HF atmosphere and the purification of these materials. There is a resistance heated zone refiner for the purification of low melting point fluorides. There is also a dry box for handling deliquescent halides and fluorides and some equipment for pulverizing and classifying flame fusion oxide feeds.

2. The crystal growth facilities include 8 baths for growth from aqueous solution. A Tem-Press 2-reactor system capable of operating at temperatures up to 800°C and pressures of 10,000 p. s. i. is available for hydrothermal growth from aqueous solutions. Halide crystal growth is accomplished with a low-temperature Bridgman furnace using sealed quartz crucibles and two Czochralski furnaces with atmosphere controls. Fluoride crystals can be grown using an RF powered Bridgeman furnace and a graphite resistance-heated NRC pulling furnace. The growth of refractory oxide crystals by melt techniques is accomplished by the use of flame fusion burners and an RF powered high-temperature Czochralski furnace. To grow oxides from solutions of fluxes there is one large and two small flux furnaces and three furnaces equipped with

pullers for top-seeded solution growth.

3. Crystal evaluation is the third capability of the facility. Precision density measurements can be made with a recording balance for large specimens and a microbalance for small specimens. Precision measurements of the lattice constant in single crystals as well as powders can be made with a Norelco x-ray unit, a clinometer and an x-ray monochromator. There is also a hardness tester for single crystal evaluation. Optical measurements can be made on a Beckman DK-1 spectrometer and a Cary 14R high-resolution spectrophotometer with ultraviolet, visible and near-infrared ranges. There is also a Beckman IR-12 for the infrared, making possible measurements over the range from 1750A to 50μ. Steady-state fluorescence spectra, excitation spectra and lifetime measurements can be made over the range from 4000A to 1.2 microns at temperatures between 4^{o}K and 500^{o}K. An electron beam unit also permits cathodoluminescence measurements. X-ray and optical orientation as well as cutting, grinding and polishing of crystals can be carried out. There is also a vacuum evaporator for electroding specimens for electrical measurements and other purposes.

During the past year crystals grown for research within the Crystal Physics Laboratory have included 50 crystals of various oxides such as germanates, $BaTiO_3$, $SrTiO_3$, $KTaO_3$, and $K(Ta, Nb)O_3$ doped with various rare earth and transition metal activators which were grown for optical fluorescence research and laser host studies, and 20 crystals of $(K, Na)TaO_3$ and $K(Ta, Nb)O_3$ which were grown for research on ferroelectricity. Programs are continuing on the growth of rare earth doped $LiYF_4$ and other fluorides for fluorescence studies on laser host materials, and on the development of strain-free crystals of $RbMnF_3$ and other perovskite fluorides for fluorescence and magnetic studies.

Also during this period 13 crystals have been grown or prepared for ten groups from other departments at MIT, and 27 crystals have been produced for 22 research laboratories outside of MIT, which attests to the reputation which has been acquired by the special capabilities of this crystal growth facility.

Extensive use of the Crystal Physics Laboratory facilities by students from other laboratories has been a large factor in this operation.

Semiconducting Crystal Growth and Characterization Facility - Room 13-4122

H. C. Gatos, Professor, Metallurgy and Electrical Engineering
M. Lichtensteiger, DSR Staff, Ext. 2381
W. Fitzgerald, Technician, Ext. 6902
T. Stewart, Technician, Ext. 6904

The Central Facility operation under the supervision of the Electronic Materials Group continues to contribute substantially through its crystal growing facilities, crystal characterization facilities, microscope facilities and high and ultra-high vacuum facilities. Semiconductor single crystals of Ge, Si, InSb, GaAs, GaSb and PbSe were provided to the various groups of the Center for Materials Science, as well as to other groups not located in the Center itself. Services were rendered to the following research groups: Ceramics, Physics of Solids, Electron Optics, Infrared, Semiconducting Device, Chemical Metallurgy and Solid State Physics. In the past year a Bridgman crystal growth facility has been added in which high quality PbSe single crystals have been grown for the Electrical Engineering Department. PbSe single crystal thin films gave been produced by sputtering on sodium chloride and glass substrates.

Characterization of semiconducting materials by means of Hall measurements and resistivity measurements were routinely performed. The facility was also made available to individuals in the various departments for their own research.

The vacuum facility is functioning in two ways, a) by providing advice in the construction and maintenance of vacuum systems and b) by providing high and ultra-high vacuum facilities for the production of thin films and for the investigation of materials under reduced pressure.

The facility is equipped to provide:

Growth from the melt under controlled conditions (pure or doped crystals) of nonvolatile elemental and compound semiconductors.

Growth of materials containing volatile constituents employing two temperature principles (closed systems).
Growth of heterojunctions by back-melting techniques.
Growth by evaporation under reduced pressures.
Growth by vapor transport.
Cutting or dicing of semiconductor crystals with single or multiple cuts.
Polishing of crystal sections.
Electrical characterization by Hall measurements.
Resistivity profiling by macro and micro-four point probe.
Chemical characterization by etching.
Microscope examination by reflected and transmitted light.

Semiconducting Crystal Preparation Facility - Room 13-3023

R. H. Rediker, Professor, Electrical Engineering
R. B. Adler, Professor, Electrical Engineering
W. Pitkin, Technician, Ext. 6844

A semiconductor sample preparation facility has been established. Materials with various physical properties can be cut by judicious choice of the two string saws, the spark cutter, or the diamond cutoff wheels which are available. Facilities for polishing and simultaneously mechanical polishing and etching, and for sandblasting are also available.

Metal Crystal Growth Facility - Room 8-402

M. C. Flemings, Associate Professor, Metallurgy, Ext. 3233/4
R. Berry, Technician, Ext. 3834

The facility is able to grow high purity metal crystals ranging in melting point from that of lead to that of tungsten, i.e.: 327.43°C to 3370°C. Alloy single crystals of the same metals can also be grown. Controlled orientation of alloy single crystals and bi-crystals can be accomplished and lamellar composite eutectic and eutectic-like crystals grown. Additionally, small to medium size quantities of high purity alloys in polycrystalline form can be prepared.

Equipment used in the facility include an electron beam crystal growing furnace, a high frequency vertical floating zone and horizontal crystal growing unit, a horizontal unit for crystal growing in a magnetic field and several resistance heated inert atmosphere crystal growing furnaces. There is a levitation melting apparatus which includes a splat cooling device. Additionally, there is an induction vacuum melting and pouring furnace and an air melting and pouring furnace.

Other equipment include a Bridgman furnace for crystal growing at $< 10^{-6}$ torr, for crystals of melting point up to 1700°C and up to 2" diameter. An arc melting furnace is available for preparation of small samples of high purity polycrystalline alloy, and for metal crystal growth of alloys and intermetallics of high melting point and high vapor pressure.

During the past year 14 types of crystals have been grown and alloys have been prepared for groups in the Department of Metallurgy, the Department of Mechanical Engineering, and the Department of Physics.

Metal Crystal Preparation Facility - Room 13-5082

B. L. Averbach, Professor, Metallurgy, Ext. 3320
G. Pishenin, Engineering Assistant, Ext. 6924

The facility has x-ray equipment for the orientation of crystals. The equipment has a Polaroid back which makes it possible to obtain a Laue photograph within a relatively short time.

Crystals are cut on a Felker unit which is equipped with a goniometer and a variety of cut-off wheels. A Servomet spark cutter and a string saw are also available. Since the cutting operation may introduce considerable local damage, metallographic equipment and annealing furnaces are available for the production of strain-free surfaces. Metallographic equipment is available for the examination of the cut surfaces.

The facility's technician either performs all the work or he supervises students who wish to orient and cut their own crystals. Staff members are available for consultation on special problems.

Central Facility for Microscopy and Metallography-Room 13-5077

J. F. Breedis, Assistant Professor, Metallurgy, Ext. 6938
R. Goss, Technician, Ext. 2447

The facility is comprised of equipment for metallographic studies using optical microscopy, electron microscopy, and electron diffraction. Routine investigations of short duration may be performed by a technician working for the facility. Instruction in the use of the electron microscope is provided for those who plan more protracted research programs. The personnel of the facility are available for advice on specimen preparation and the interpretation of results.

The equipment available includes a Siemens Elmiskop I electron microscope with high resolution electron diffraction attachment, a Leitz MM5 metallographic microscope, and Spencer and Unitron stereo microscopes. Specimen preparation facilities include two vacuum evaporators and several types of thin foil preparation devices. A photographic darkroom and enlarger is associated with the facility.

Gas Analyzer Mass Spectrometer Facility-Room 8-109

J. F. Elliot, Professor, Metallurgy, Ext. 3305

A gas analyzer is used to analyze the molecular beam from a Knudsen or Langmuir effusion cell. This small mass spectrometer is suitable for the identification of vapor species, and under limited conditions, for determination of ratios of concentrations of vapor species.

X-ray and Low Energy Electron Diffraction Laboratory-Room 13-2106

D. P. Shoemaker, Professor, Chemistry, Ext. 6827

A General Electric XRD-5 x-ray Diffractometer with two x-ray tubes is available for taking x-ray diffraction photographs as needed for structure investigations or for orienting crystals. If the user does not have his own diffraction equipment, other equipment in the laboratory can generally be borrowed including a back reflection Laue camera with a Polaroid film cassette.

The laboratory also has a Varian Low-Energy Electron Diffraction Unit, complete with test chamber, vacuum system, bakeout oven, and all needed gauges and controls. It can be used for low-energy electron diffraction studies of ultra-clean surfaces of crystals and of chemisorbed layers.

In all cases the user of these equipments is expected to do all his own crystal preparative and manipulative work, supply other needed materials and do his own result interpretation.

X-ray and Electron Optics Laboratory Facility - Room 13-4009

R. E. Ogilvie, Professor, Metallurgy, Ext. 3311
T. O. Ziebold, Associate Professor, Nuclear Materials, Ext. 6885
J. Adario, Technician, Ext. 6887

The X-ray diffraction central facility will continue to offer the services performed in the past. These services have consisted of teaching graduate students and technicians from other departments in the Institute to carry out routine X-ray diffraction studies. The facility has also used its own personnel to perform the necessary experiments for members of the Institute. Most of this work has consisted of orienting single crystals, identifying unknown materials and precision lattice parameter measurements.

The electron microanalyzer has become a general service instrument for the Materials Science Center. Examples of the work that this instrument is well suited for includes analysis of diffusion couples, distribution of elements in areas of dendritic segregation, identification of inclusions, and the analysis of thin films.

The laboratory has just installed a new scanning electron microscope which will be made available to the members of the Institute. This instrument is well suited for the study of irregular or fractured surfaces.

Central Computation Facility - Room 13-5145

B. L. Averbach, Professor, Metallurgy, Ext. 3320
R. Kaplow, Associate Professor, Metallurgy, Ext. 3322
J. W. Brackett, Research Associate, Metallurgy, Ext. 6919
Barbara Boudreau, DSR Staff, Ext. 6928

The facility is equipped with an IBM 1050 console, a remote terminal which may be linked to the time sharing system (CTSS) at either the MIT Computation Center of Project MAC. Time sharing users may also utilize an available "ARDS I" storage tube display unit, for dynamic display of graphical and other pictorial information. IBM type 029 and type 026 keypunch units (keypunch) are available for card punching for "off-line" input to the time sharing systems or for batch processing input.

All of the facilities of CTSS are available through the typewriter-storage display console including those which allow program editing, compilation and execution (with languages such as MAD, Fortran and AED). System MAP is also available, which allows a wide variety of mathematical analyses to be performed without any programming. The latter system has been extended and now includes, in addition to previous facilities, a package of efficient matrix operation routines and simple commands for graphical display on the storage tube.

Mrs. Barbara Boudreau is the programmer associated with the facility. Mrs. Boudreau is available for consultation regarding the use of the time sharing system and the batch processing system as well as for assistance in actual programming difficulties.

During the past year, many interesting problems have been analyzed with the assistance of the center, often by persons who had little or no previous experience in computer applications. The variety of these, reflecting the wide range of interests within materials research, is evidenced by a brief sampling of topics: the scattering of light from fluids near critical points, structural studies of alloy phases, the effect of pH and metal ion concentration on equilibirum hydrolysis, and the performance characteristics of germanium bolometer detectors.

Materials Center Reading Room - Room 13-2137

Alice McGee Robrish, Librarian, Ext. 6840

The Reading Room has a very selective working collection oriented toward materials science. Immediate availability of items in the collection is of prime concern and it is therefore a reserve collection circulating only during hours that the Reading Room is closed.

There are 850 monograph titles and subscriptions to 80 journals. Normally journal titles include only the last two years of issues.

There is a Xerox facility located across the hall available to those who can charge copies to an operating account.

The services of the Reading Room include literature searching, bibliographies, and aid in maintaining current awareness. A bulletin is periodically published giving an annotated listing of recent acquisitions, library news, and information on science literature. Further, the Reading Room serves as a liaison between Materials Center personnel and the Defense Documentation Center, referral services, and specialized data analysis centers.

Technical Information Services - Room Lincoln D-209

E. P. Warekois, Research Staff, Lincoln Laboratory and National Magnet Laboratory, Ext. 81450

Mr. Warekois provides technical information service on materials to the Center for Materials Science and Engineering, the MIT Lincoln Laboratory and the National Magnet Laboratory.

Academic Staff

who have received partial support from ARPA Contract SD-90

during the period 9/16/66 - 9/15/67

D. Adler, Assistant Professor, Electrical Engineering
R. B. Adler, Professor, Electrical Engineering
B. L. Averbach, Professor, Metallurgy and Materials Science
F. O. Arntz, Assistant Professor, Electrical Engineering
G. B. Benedek, Professor, Physics
J. F. Breedis, Assistant Professor, Metallurgy and Materials Science
R. A. Brown, Assistant Professor, Metallurgy and Materials Science
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P. D. DeCicco, Assistant Professor, Physics
D. J. Epstein, Professor, Electrical Engineering
M. C. Flemings, Professor, Metallurgy and Materials Science
H. C. Gatos, Professor, Metallurgy and Materials Science
C. W. Garland, Professor, Chemistry
T. J. Greytak, Professor, Physics
J. D. Litster, Professor, Physics
F. R Morgenthaler, Professor, Electrical Engineering
S. C. Moss, Associate Professor, Metallurgy and Materials Science
D. H. Navon, Associate Professor (Visiting), Electrical Engineering
G. W. Pratt, Professor, Electrical Engineering
R. H. Rediker, Professor, Electrical Engineering
R. M. Rose, Associate Professor, Metallurgy and Materials Science
K. C. Russell, Assistant Professor, Metallurgy and Materials Science
M. O. Scully, Assistant Professor, Physics
D. J. Sellmyer, Assistant Professor, Metallurgy and Materials Science
A. Smakula, Professor, Electrical Engineering
R. A. Smith, Professor, Physics
R. D. Thornton, Associate Professor, Electrical Engineering
D. R. Uhlmann, Assistant Professor, Metallurgy and Materials Science
R. B. Williamson, Assistant Professor, Civil Engineering
A. Witt, Associate Professor, Metallurgy and Materials Science
J. Wulff, Professor, Metallurgy and Materials Science
Y. Yacoby, Assistant Professor, Electrical Engineering

Research Reports

CHEMICAL AND SOLID-STATE PHYSICS

SOLID STATE MOLECULAR THEORY GROUP

Personnel

Professor J. C. Slater, Institute Professor, Emeritus, Physics
Professor G. F. Koster, Professor, Physics
* Professor P. D. DeCicco, Assistant Professor, Physics
Dr. A. J. Freeman, Associate Director, National Magnet Laboratory
(Now Head of the Physics Department, Northwestern University)
Dr. A. Kitz, Visiting Scientist, Physics
(Now at the University of Hamburg, Germany)
D. S. Becker, Research Assistant, Physics
J. W. Gadzuk, Graduate Student, Mechanical Engineering
R. Gilmore, Instructor, Physics
J. F. Kenney, Research Assistant, Physics
(Now at the University of Edinburgh, Scotland)
D. Koelling, Graduate Student, Physics
B. Mayes, Graduate Student, Physics
W. E. Rudge, Research Assistant, Physics
J. Sokoloff, Graduate Student, Physics
(Now at Brookhaven National Laboratory)
Josephine Shea, Secretary, Physics

Degrees Granted

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

Sponsorship

Office of Naval Research, Nonr-1841(34), DSR 70280
National Science Foundation, NSF-GP-3241, DSR 75251
National Science Foundation, NSF-GP-7677, DSR 70607

Research Report

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

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

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

P. DeCicco, A Note on the ℓ-Convergence of the APW Method, 65.

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

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

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

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

R. Gilmore, Branching Diagrams, 64.

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

R. Gilmore, Stellar Maser, 66.

R. Gilmore, Darwin Again, 66.

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

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

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

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

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

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

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

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

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

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

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

Publications

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

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

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

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

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

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

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

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

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

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

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RADIOFREQUENCY, MICROWAVE AND OPTICAL SPECTROSCOPY OF LIQUIDS, SOLIDS AND GASES

Personnel

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

Personnel who have left during the period

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

Degrees Granted

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

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78880, DSR 75102
Sloan Fund for Basic Research in the Physical Sciences (Sloan Fund 27731)
National Aeronautics and Space Administration, NGR-22-009-182, DSR 76375

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

1.0 Brillouin Scattering in Liquids, Solids, and Gases

1.1 Brillouin Scattering Near the Critical Point of NH_4Cl

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

Object:

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

Research Report

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

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

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

Research Report

Using the modified "Michelson scheme" devised by Dr. Paul Smith

of the Bell Telephone Laboratories, we have succeeded in putting into operation of long, single mode laser capable of delivering between 10 and 25 milliwatts of power. By piezo electric control of the mirrors and thermostatic control of the laser mount we have been able to secure operation of this single moded laser stabilized in frequency to ~ ± 10MHz over periods of several hours. This laser is now being used to study the lifetimes of thermally excited phonons in NH_4Cl near room temperature.

1.3 Lifetimes of Hypersonic Sound Waves in Solid

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

Object:

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

Research Report

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

1.4 Brillouin Scattering in Gases

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

Object:

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

Research Report

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

1.5 Brillouin Scattering in Liquid Helium

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

Object:

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

Research Report

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

increasing our resolution in order to measure line widths, and on increasing our signal strength for greater accuracy.

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

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

Object:

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

Research Report

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

1.7 Brillouin Spectrum of a Fluid Near its Critical Point

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

Object:

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

Research Report

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

1.8 Heterodyne Detection of the Rayleigh and Brillouin Spectrum

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

Object:

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

Research Report

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

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

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

Research Report

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

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

2.0 Scattering of Light from Transparent Ferromagnets

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

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

Object:

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

Research Report

We have constructed and put into operation a high-resolution Fabry-Perot interferometer, a cooled housing for a near infrared photomultiplier tube, and have assembled a pulse height discrimination system. This system enables us to detect photocurrents as low as one electron per second. We have used ti in conjunction with a Nd^{3+}: YAG laser at 1.06μ to detect the light scattered by thermal sound waves in water and KCl. The light scattered by magnetoelastic waves in YIG will

be only slightly less intense, but we have been unable to detect it with our present samples because of the very intense scattering from imperfections. With improved samples we shall search for light scattered by acoustic magnons, phonons, and magnetoelastic waves in yttrium iron garnet.

2.2 Faraday Rotation in $CrBr_3$

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

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

We have assembled a dewar and temperature control system capable of operating from $4.2^{\circ}K$ to room temperature, along with an optical system that enables us to measure the plane of polarization to within 0.003°. Using this system we have observed the susceptibility of $CrBr_3$ to increase by a factor of 50 near the critical temperature. We are now studying the detailed nature of the divergence of the susceptibility and plan to extend our measurements to other ferromagnetic materials.

Theses

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

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

Publications

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

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

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

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

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LOW TEMPERATURE PHYSICS

Personnel

** Dr. C. A. Shiffman, DSR Staff, Center for Materials Science and Engineering
** Dr. J. E. Neighbor, DSR Staff, Center for Materials Science and Engineering
Dr. R. C. Williamson, DSR Staff (Guest) Center for Materials Science and Engineering
** P. H. Haberland, Research Assistant, Physics
** J. W. McWane, Research Assistant, Physics
Daryl A. Carnam, Research Assistant, Metallurgy
M. E. Malinowski, Senior Student, Physics
J. Michelson, Senior Student, Physics
J. Sandusky, Senior Student, Physics
** H. Cronin, Technician, Center for Materials Science and Engineering
* Gladys Lucian, Secretary, Center for Materials Science and Engineering

Personnel who have left during the period

R. S. Newbower, DSR Staff (Now Graduate Student at Harvard University)
R. F. Tinker, NSF Graduate Fellow (Now at R. L. E., MIT)
M. E. Malinowski, Senior Student (Now at University of Illinois)
J. Michelson, Senior Student (Now at University of Wisconsin)
J. Sandusky, Senior Student (Now at University of Maryland)

Degrees Granted

M. E. Malinowski, B.S., June 1966
J. Michelson, B.S., June 1966

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78880, DSR 75101

1.0 The Specific Heat of Superconductors

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

In collaboration with Professor H. C. Gatos we have been measuring the specific heats of a series of transition metal carbides. A complete report on these activities is contained in Section 2.1 of the Electronics Materials Laboratory report (H. C. Gatos).

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

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

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

tial behavior is observed in the temperature dependence; if ω is beyond the plateau various degrees of anomalous behavior are found.

The key to the understanding of these observations is the fact that in very pure metals an electron may make many cyclotron orbits before scattering, and hence may ultimately arrive in the skin layer out of phase with respect to the r.f. field. We have exploited this idea in a simple path-integral calculation of the strength of the resonance couched in terms of the quantities $x \equiv \pi/\omega_c\tau$ and $\theta \equiv 2\pi\omega/\omega_c$. The theory gives very good agreement with the observed dependencies on ω and τ. From the frequency dependence it is possible to extract fairly accurate estimates (i.e. 30 to 50%) of ω_c and τ at a given temperature, and from the temperature dependence one can determine the relationship $\tau(T)$. Values of effective mass deduced from ω_c and the field at which the resonance occurs agree quite well with data from cyclotron resonance and de Haas van Alphen experiments. Values of τ are in keeping with estimates based on the d.c. conductivity, but show a strong (up to a factor of 6) variation from one extremal orbit to another on the Fermi surface.

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

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

Research Report

Newbower and Neighbor recently reported the discovery of an anomaly in the electrical resistance of large single crystals of very pure gallium. They found that the resistance in zero magnetic field has a narrow plateau near 1.7°K, which is displaced to lower temperatures as the field is increased. We have carried out very precise calorimetric measurements which show that there is no corresponding anomaly in the specific heat of gallium. In these measurements our specimen was a cylindrical single crystal composed of 7.9 moles of "super pure" metal obtained from the same source as that used by

Newbower and Neighbor. Its heat capacity, C, was measured using the continuous-warming method and apparatus developed previously in this laboratory. Several high-resolution runs (temperature steps less than $0.005^{o}K$) over the temperature range $1.1-2.3^{o}K$ failed to disclose any significant fine structure in the function C(T). In view of the depression of the resistive anomaly to lower temperatures with increasing magnetic field it was clearly advantageous to compare heat capacity data taken in zero field with data taken in various external fields. If the anomaly were indeed caused by a phase transition such a comparison would indicate directly the associated change of entropy, ΔS. On the contrary our results establish the very small upper limit $\Delta S/\gamma T \leq 6 \times 10^{-5}$, where γT is the normal electronic entropy.

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

4.0 Properties of Metals at High Pressures and Low Temperatures

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

Research Report

We have previously described a novel high pressure-low temperature apparatus which uses a bellows pressurized with liquid helium to drive a piston intensifier immersed in the helium bath. Solid helium is used as the pressure transmitting "fluid". In this apparatus the only connection between the high and low temperature parts of the system are the capillary tubes carrying relatively low pressures to the bellows and sample space. In the past year a number of experiments have been done to check the accuracy and reproduceability of the system as a whole, to test the reliability of the bellows assembly and to explore the nature and

magnitude of the strains on psecimens in the quasi-hydrostatic environment in the high pressure chamber.

The bellows functioned perfectly in 80 cyclings to full pressure at 4.2°K or below over the course of the year. In every respect their performance was ideal, except for a small but reproduceable hysteresis, in the effective spring constant. These observations commend the bellows principle to applications where uni-axial stress is desired. In particular, for experiments on metals where large strains are not encountered, a bellows apparatus would be especially simple and advantageous. (Our system required four bellows in series because of the high compressibility of solidified gases.) The complete system did not operate as well as could be hoped, however. This was almost entirely due to the difficulty in making good, low friction seals between the intensifier piston and the walls of the high pressure chamber. With indium packing, leak-tight sliding joints could be made if the bore of the bomb was kept free of scratches and other distortions by occasional reaming. Friction corrections were substantial, but since they would be determined to about ± 80 atmos. they were not a major factor in the accuracy of pressure measurements.

By far the most serious problem was the lack of true hydrostatic conditions in the bomb. (This filing is characteristic of all piston type systems using solidified gases as the pressure transmitting medium.) In order to explore this we have made measurements of the shift in transition temperature of indium with pressure, using solid-helium as the transmitting "fluid". Three techniques were used: (1) d.c. electrical resistance (2) mutual inductance at 23 cps of a coil system containing the specimen, and (3) surface impedance at 700kHz. In all three types of experiment the values of the shift in T_c agreed with each other and with curves taken from the literature. The width of the transition appears to increase with increasing frequency, however. Since the frequency determines the depth of penetration of the measuring currents (in the normal state) these results indicate that there is a strong gradient in the strain at the surface of the specimen. We also observe that ΔT_c is not a sensitive function of pressure near 3,000 atmospheres, which implies that most of this gradient is developed in the initial stages of compression of the solid helium, where the largest internal displacements occur.

Publications

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

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

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

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

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

SEMICONDUCTORS AND INFRARED SPECTROSCOPY

Personnel

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

Sponsorship

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

Research Report

1.0 Spectroscopy in the Very-far Infrared

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

The transmittance spectra of two far-infrared long-wave pass filters of the powdered salt in polyethylene type first described by Yamada et. al. were measured at 296°, 77°, and 4.2°K. Such filters are required to prevent radiation of wavelength less than a particular value from entering an optical system, and must function without a light leak in the opacity region, with a sharp cut-on characteristic, and with high transmittance toward longer wavelengths in the pass-region. For the use with a cryogenic bolometer detector (see below) these properties were required at liquid helium temperature to eliminate undesired

radiation from the room and other sources. These filters performed very satisfactorily, with a significant gratuitous improvement at low temperatures in their cut-on and transmittance characteristics relative to that at room temperature. The filters are made by laminating in a heated press thin polyethylene sheets each containing one of five or six different far-infrared reststrahlen-active salts, uniformly dispersed. The filter containing NaCl, KCl, KBr, KI and CsBr showed at 4.2°K a cut-on at 124 μm, and a sharp rise in transmittance, the "knee" ending at ~165 μm, and the transmittance reaching a maximum of 77% beyond 200 μm. The second filter containing an additional CsI lamination, showed at 4.2°K a cut-on at 147 μm, again a sharp rise, the "knee" now ending at ~190 μm and the transmittance maximum reaching 65% beyond 200 μm.

(b) Detectors for the very-far infrared

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

A bolometer based on these principles has been constructed and carefully tested at 1.5°K. Absolute measurements of the 500°K blackbody responsivity, noise spectrum and detectivity for $\lambda > 150\,\mu$m, their variations with frequency from 25-1000 Hz, the optimum bias current and the associated time constant, as well as the thermal parameters of the

bolometer have been made. The bolometer behaves very much as was expected from its design. It has a far-infrared detectivity $D = 5 \times 10^{11}$ $Hz^{1/2}/W$ at 400 Hz, rising to 6.2×10^{11} $Hz^{1/2}/W$ at 1 kHz, and a response time constant of 230μs. This bolometer when used with a suitable preamplifier allows operation beyond the "1/f" noise regions of both detector and preamplifier. A specially-designed ultra-low noise preamplifier has been constructed and tested along with the bolometer, yielding very satisfactory results.

2.0 Far-infrared Absorption in Semiconductors

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

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

Meeting Papers

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

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

Publications

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

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

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

ORDER-DISORDER PHENOMENA

Personnel

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

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75104, 78880
National Science Foundation Grant, GP-5042, DSR 76047
Research Laboratory of Electronics, supported by the Joint Services Electronics Program under Contract DA36-039-AMC-03200(E).

Research Report

1.0 Ultrasonics

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

During our high-pressure work on NH_4Br at low temperatures, a new ordered phase was discovered in the region $T \sim 180$ to $230^{\circ}K$ and $p > 2000$ bar. The acoustic properties of this phase were completely determined, and the regions of the phase-transition lines were carefully

studied. Data are now available on the previously known disordered cubic-ordered tetragonal lambda transition as well as the new order-disorder lambda transition and the order-order transition between the new high-pressure phase and the low-pressure tetragonal phase. X-ray and infrared data have also been obtained at 1 bar for temperatures down to 20°K. In contrast to the much simpler system NH_4Cl, the NH_4Br results clearly show that many complexities can occur in cooperative phenomena involving orientational ordering.

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

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

Interest in the liquid-vapor critical point is still very great, and work is in progress on xenon near its critical point at 16.6°C and 58 bar. Recent measurements on helium suggest that the adiabatic sound velocity goes to zero at a critical point, in contradiction to the classical theoretical

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

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

2.0 Infrared Spectroscopy

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

The spectra contain several features which are very sensitive to the structural and ordering changes occuring at this lower transition and permit us to clarify its detailed behavior.

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

Publications

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

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

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

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

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Sponsorship

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

Research Report

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

Sponsorship: Army Research Office, Durham

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

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

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

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

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

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

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

Sponsorship: Humble Oil and Refining Company

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

3.0 Low-Energy Electron Diffraction (LEED)

Sponsorship: National Science Foundation, Advanced Research Projects Agency

The rebuilding of our apparatus for low-temperature work on surfaces produced by cleavage has been completed, but we find it necessary to replace the fluorescent screen before work on physical absorption of noble gases on vacuum-cleaved zinc (0001) surfaces can commence.

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

Publications

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

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

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

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

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

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

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

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

ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES OF MATERIALS AND DEVICE APPLICATIONS

MATERIALS THEORY GROUP - Electric, Magnetic, and Optical Properties of Materials

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Degrees Granted

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G. M. Bunce, S.B., Electrical Engineering, September 1967

Sponsorship

Office of Naval Research, Nonr-1841(72); NRO18-106, DSR 78721
Advanced Research Projects Agency, SD-90, DSR 78881, 78891
Army Research Office(Durham), DA-31-124-ARO(D)-92, DSR 79489

Research Report

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

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

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

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

depends on external pressure the high pressure phase change observed in the Pb salts can be explained.

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

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

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

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

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

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

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

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

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

Narrow Energy Band Theory

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

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

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

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

Theses

G. M. Bunce, "Laser Action in a Stressed Semiconductor", S.B. Thesis, Department of Electrical Engineering, September 1967.

H. P. H. Yuen, "Quantum Statistical Theory of Phase Transition in a Spin Model", S.B., S.M., and E.E. Thesis, Department of Electrical Engineering, September 1967.

Publications

D. Adler, "Theory of Semiconductor-to-Metal Transitions", (with H. Brooks), Phys. Rev. 155, 826 (1967).

D. Adler, "Semiconductor-to-Metal Transitions in Transition Metal Compounds", (with J. Feinleib, H. Brooks and W. Paul), Phys. Rev. 155, 851 (1967).

D. Adler, "The $Ti_{2x}V_{2(1-x)}O_3$ System", Bull. Am. Phy. Soc., 12, 328 (1967).

D. Adler, "Properties of Transition Metals and Alloys", Magnetism and Magnetic Materials Digest, W. D. Doyle and A. B. Harris, eds., Academic Press, New York, 1967, p. 50.

D. Adler, "Transition Metal Oxides", Solid State Physics, F. Seitz, D. Turnbull, and H. Ehrenreich, eds., Academic Press, New York, Vol. 21 (to be published).

L. W. Gruenberg, "LT10", Low Temperature Conference in Moscow, Physics Today. 20-4, 97 (1967).

L. W. Gruenberg, "Josephson Tunneling in Superconductors", Los Alamos Scientific Report LAMS 3414, (1967).

L. W. Gruenberg, "Bose Einstein Condensation and Superconductivity", Los Alamos Scientific Report LAMS 3600 (1967).

L. W. Gruenberg, "Recent Developments in the Theory of Phase Transitions", Los Alamos Scientific Report LAMS 3805 (1967).

G. W. Pratt, Jr., "The Materials Game - An APW Analysis of the Lead Salts", Academic Press, Inc. 1966.

G. W. Pratt, Jr., and N. J. Parada, "Interband Momentum Matrix Elements and a $\vec{k} \cdot \vec{p}$ Interpolation Method Applied to PbTe", Academic Press, to be published.

J. E. Ripper and C. G. Whitney, "Frequency Modulation and Demodulation of a Gallium Arsenide Injection Laser Using Ultrasonic Waves", IEEE Journal of Quantum Electronics, Vol. QE 3, pp. 202-203, May 1967.

SEMICONDUCTOR MATERIALS AND DEVICES

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* Professor D. H. Navon, Associate Professor (Visiting) Electrical Engineering
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H. St. Onge, Teaching Assistant, Electrical Engineering
T. E. Sharon, Undergraduate Student, Electrical Engineering
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* C. R. Grant, Engineering Assistant, Electrical Engineering
* Dorothy Chapman, Technician, Electrical Engineering
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* Berylee Schutz, Secretary (part time), Electrical Engineering
Jarmila Z. Hrbek, Secretary (part time), Electrical Engineering
* Jean Gorrasi, Secretary (part time), Electrical Engineering

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E. D. Crosby, Research Assistant (Now at General Electric Company)
C. K. Erdelyi, Research Assistant (Now in industry)
D. C. Green, Research Assistant (Now at Sanders Associates)

S. H. L. Liu, Research Assistant (Now in doctoral study, Harvard University)

E. A. Miller, Research Assistant (Now at Fairchild Semiconductor, Inc.)

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G. S. Almasi, Ph.D., Electrical Engineering, February 1967

A. W. Carlson, Ph.D., Electrical Engineering, June 1967

J. Shah, Ph.D., Physics, February 1967

D. L. Smythe, Ph.D., Electrical Engineering, February 1967

M. S. Adler, S.M., and E.E., Electrical Engineering, June 1967

J. G. Calderone, S.M., Electrical Engineering, September 1967

C. K. Erdelyi, S.M., Electrical Engineering, September 1967

C. R. Hewes, S.M., Electrical Engineering, February 1967

J. G. Kassakian, S.M. and E.E., Electrical Engineering, September 1967

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

E. A. Miller, S.M., Electrical Engineering, June 1967

P. E. Norris, S.M. and E.E., Electrical Engineering, June 1967

J. A. Rome, S.M. and E.E., Electrical Engineering, September 1967

P. S. Showman, S.M., Electrical Engineering, September 1967

S.M. Spitzer, S.M. and E.E., Electrical Engineering, June 1967

H. St.Onge, S.M. and E.E., Electrical Engineering, June 1967

E. D. Crosby, S.B., Electrical Engineering, June 1967

D. C. Green, S.B., Electrical Engineering, June 1967

T. E. Sharon, S.B., Electrical Engineering, February 1967

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78881, 75112, 75115, 75119
U. S. Army Electronics Command, DA-28-043-AMC-01978E, DSR 76252
National Aeronautics and Space Administration, NsG-496(part), DSR 76153, 76167, 76191
National Aeronautics and Space Administration-Electronics Research Center, NgR 22-009-234, DSR 70574
Office of Naval Research, Nonr-1841(51), DSR 77984; NOOO 14-67-A-0204-0010, DSR 70421
U. S. Department of Commerce, Northeast Corridor Transportation Project, C-85-65, DSR 76104
Ford Foundation Fellowship
NSF Fellowship
NSF Traineeship
NSF Research Initiation Grant, DSR 70393
GM Fellowship
MIT Sloan Fund for Basic Research

Research Report

Survey

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

1.0 Effects of Electric Field on Optical Absorption

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

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

Sponsorship: Advanced Research Projects Agency

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

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

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

these levels and values of various parameters have been determined.

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

1.2 Electro-Reflectance in GaAs

Personnel: Professor F. O. Arntz; T. E. Sharon

Sponsorship: Advanced Research Projects Agency

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

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

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

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

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

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

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

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

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

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

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

Sponsorship: National Aeronautics and Space Administration

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

1.5 Optically Pumped Absorption in II-VI Compounds

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

Sponsorship: Advanced Research Projects Agency

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

1.6 Electro-Reflectance in CdS

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

Sponsorship: National Aeronautics and Space Administration

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

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

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

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

Sponsorship: Advanced Research Projects Agency

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

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

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

3.0 Effects of Strain from Passivating Layers on Silicon

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

Sponsorship: Advanced Research Projects Agency

A preliminary evaluation has been made by Mr. Serebrinsky of the interaction between a semiconductor and its passivating insulator via the stress fields usually present at the interface. A facility for depositing silicon nitride films by pyrolitic decomposition of silane was set up (in cooperation with Mr. J. M. Harris of Electronics Materials Group), and

films were subsequently deposited on silicon; some additional time was devoted to the control of the film and calibration of the equipment. The character (elastic or plastic) of the deformation produced by the mismatch of expansion coefficients is currently under study.

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

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

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

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

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

4.0 Thermophotovoltaic Energy Conversion

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

Sponsorship: U. S. Army Electronics Command

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

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

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

5.0 High Injection Effects in Semiconductors

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

Sponsorship: U. S. Army Electronics Command

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

An investigation of the effect of carrier-carrier scattering on the

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

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

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

6.0 Nuclear Magnetic Resonance in Lead Telluride

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

Sponsorship: Office of Naval Research, and BTL Fellowship

Our study of the carrier-dependent shifts of the Pb^{207} and Te^{125}

nuclear magnetic resonance (NMR) lines in n- and p-type PbTe has comtinued on several fronts. Measurements on our original pair of samples of the temperature dependence of the shifts between 77°K and room temperature are nearly complete. These measurements have been made in cooperation with Drs. P. L. Sagalyn and J. A. Hofman of the Army Materials Research Center. An elementary theory based on the changing degeneracy of the carriers with temperature appears to account qualitatively for the observed temperature dependences: but quantitative tests of this theory await completion of the data taking.

Progress on our own NMR facility has been such that we can now observe Pb^{207} resonances in PbTe; however, further improvements in sensitivity are still required. We have just obtained an excellent phase-locked radio receiver which will be the nucleus of a new rf bridge spectrometer now being built by Mr. Siegel.

We have begun a program of sample preparation and evaluation, so that the effects of variations in carrier concentrations can be studied in more detail. Hall coefficient, resistivity and thermoelectric power will be measured in each new sample before it is used in an NMR measurement.

As a corollory to the NMR program in PbTe, we have completed two studies of NMR instrumentation techniques. Mr. M. Adler has carried out an experimental and theoretical study of the operation and sensitivity of transistorized NMR spectrometers. He has also completed the design and construction of a field-tracking NMR gaussmeter. An account of this work may be found in Mr. Adler's S. M. Thesis.

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

7.0 Graded Energy Gap Photovoltaic Device

Personnel: Professor A. C. Smith; G. S. Almasi

Sponsorship: National Aeronautics and Space Administration

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

This paper reports the results of measurements on photovoltaic devices made by the interdiffusion of CdTe and HgTe. It is found that the devices display rectification and possess a spectral response which decreases exponentially with decreasing energy from a maximum at the energy corresponding to the CdTe bandgap (1.5 eV). The theoretical model developed to account for this behavior involves a sandwich of constant energy-gap material and graded-gap material, with a p-n junction in the constant-gap material immediately adjacent to the graded region. The exponent of the spectral response is then found to reflect the band-edge variation of the carrier species being collected by the junction. The devices may be useful as detectors in application where long wave-length response and a short response time (theoretically below 10^{-8} sec) are more important than senstiivity (10^{-3} μV/μW at most). They are also fairly sensitive in a narrow spectral region (1.4 eV - 1.5 eV) just below the CdTe bandgap energy (noise-equivalent-powers down to 2×10^{-9} watts/cps). However, because the spectral bandwidth is so narrow, the devices in their present from offer no improvement over present photovoltaic energy converters. To improve their performance as photodctectors a more precise control of the equilibrium carrier concentrations must be developed.

8.0 Cadmium - Zinc Antimonide Solid Solutions

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

Sponsorship: National Aeronautics and Space Administration

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

Electrical and op ical measurements have been made on p-type single-crystal ZnSb, CdSb, and $Cd_xZn_{1-x}Sb$ alloys. For each crystal

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

9.0 Galvanomagnetic Measurements in High-Resistivity Materials

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

Sponsorship: National Aeronautics and Space Administration

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

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

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

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

10.0 Microelectronics

Personnel: Professor D. Navon; P. Showman

Sponsorship: Advanced Research Projects Agency

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

11.0 Solid State Switching

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

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

Professors Thornton and Navon are continuing their work on power machinery utilizing kilowatt solid-state commutation. Mr. Erdelyi has completed the construction and testing of an unconventional electric motor yielding high mechanical power output per unit weight. Problems connected with the construction of high-power transistors to provide solid-state commutation for this machine were pursued by Messrs. Miller, Lichtenberger, Spitzer and Lindsey. Miller has solved the time-dependent heat-flow equation in typical power transistor structures, leading us to an

understanding of the effect of transistor structure design parameters on the instability ("Second Breakdown") problem encountered in semiconductor power devices. Mr. Lichtenberger performed a similar analysis yielding additional information, by solving heat-flow problem using a distributed thermal-circuit analog and subjecting it via the AEDNET computer program. Mr. Spitzer has measured the thermal instability parameter α for transistors, and has determined a theory for poor high-voltage low-current performance of transistors, compared with their high-current low-voltage behavior. Mr. Lindsey is analyzing the saturation characteristic of power transistors with thick, high-resistivity collector regions needed for high voltage capability.

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

12.0 Thin-Film Field-Effect Devices

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

Sponsorship: Advanced Research Projects Agency

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

13.0 Study of Basic Device Parameters in the Lead Salts

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

Sponsorship: Office of Naval Research, National Science Foundation Fellowship

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

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

The diffused p-n junctions studied thus far have shown the rather poor reverse voltage-current characteristic common in lead-salt diodes. Devices will now be fabricated using annealed material of lower initial carrier concentration. Brebrick's theory of the inter-diffusion process in binary ionic semiconductors (J. Appl. Phys. 30, 311, (1959)) has been applied to predict the junction profile (spatial dependence of the deviation from stoichiometry) for a limited set of boundary conditions. These

results show significant variations in the profile for different diffusion conditions, and they will be extended to include the cases of most practical interest for correlation with diode characteristics and junction capacitances. Results of the studies on lifetime and high-field effects should also increase the understanding of p-n junction properties.

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

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

14.0 Photoluminescence from Semiconductors

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

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

The goal of this program is the study of photoluminescence in both direct-and indirect-gap semiconductors, and of ways to control this photoluminescence. Equipment is being assembled or built for use in this program. A recording prism spectrometer is now operational and has been used to measure the photoluminescent spectrum of GaS. A system for the deposition of insulating layers using the oxidation of silane has been built, and films of SiO_2 have been deposited on Ge, Si, and GaAs. An evaporator for the controlled deposition of nearly transparent metal films has just been put into operation. A tiltable furnace of the type used by Nelson has been built for the liquid epitaxial growth of III-V compounds from saturated solutions in the valence III metal. The first attempt will be to grow GaAs from Ga solutions but it is hoped the program will then

proceed to the growth of mixed crystals (e.g. $Ga_xIn_{1-x}As$).

In direct-gap semiconductors, field control of the luminescence will be studied. The effort on indirect-gap semiconductors will first concern itself with the photoluminescence from silicon for donor and acceptor concentrations of approximately 10^{16} impurities/cm^3. Experiments are being developed to observe a modulation of that photoluminescence through generation of non-equilibrium phonons.

15.0 Temperature Dependence of Optically Pumped Semiconductor Lasers

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

Sponsorship: Advanced Research Projects Agency

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

Laser action was observed in an n-type InAs sample ($N_D = 2 \times 10^{16} cm^{-3}$) in the temperature range 10 - 40°K. The temperature dependence of the threshold was found to be nearly exponential with threshold increasing from 4 to 10×10^3 A cm^{-2} in the range observed. This increase is less than has been reported for the InAs diode laser. Well above threshold the output from the InAs was found to vary linearly with the input and changed little with temperature as might be expected if the optically pumped laser is operating at the limiting maximum quantum efficiency. With the pump power available, laser action was not achieved in the several samples of p-type InAs which were investigated. In these

samples the observed spontaneous emission corresponded to conduction-band to acceptor level transitions whereas in the n-type sample the peak emission corresponded to band to band transitions.

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

16.0 Electrical and Electro-Optical Properties of Heterojunctions

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

Sponsorship: Advanced Research Projects Agency

Heterojunctions between CdTe and InSb have been fabricated by the interface alloy technique. Laue patterns of the CdTe seed and the regrown InSb were compared and showed that the InSb was single crystal and regrew with the same orientation as the seed. Kossel-line patterns indicate that the junction region is single crystalline. N-CdTe to n-InSb junctions do not exhibit rectification. A program has been initiated to convert to p-type the n-type single crystal CdTe which is available, by annealing under controlled Te vapor pressure.

Theses

G. S. Almasi, "Photovoltaic Effects in Cadmium Telluride -Mercury Telluride Heterostructures", Ph.D. Thesis, Department of Electrical Engineering, November 1966.

A. W. Carlson, "Free Carrier Absorption and Effective Masses in Zinc Antimonide-Cadmium Antimonide Alloys", Ph.D. Thesis, Department of Electrical Engineering, May 1967.

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

D. L. Smythe, "Hole and Electron Mobility in Semiconductors With Large Numbers of Excess Carriers", Ph. D. Thesis, Department of Electrical Engineering, January 1967.

M. S. Adler, "Application of R. F. Transistors to a Nuclear Magnetic Resonance Spectrometer", S. M. Thesis, Department of Electrical Engineering, June 1967.

J. G. Calderone, "Nuclear Magnetic Resonance Sensitivity Enhancement by Signal Averaging", S. M. Thesis, Department of Electrical Engineering, September 1967.

C. K. Erdelyi, "The Design of a Light Weight Medium Power Electric Motor", S. M. Thesis, Department of Electrical Engineering, August 1967.

C. R. Hewes, "A Germanium Device for Thermophotovoltaic Energy Conversion", S. M. Thesis, Department of Electrical Engineering, January 1967.

J. G. Kasakian, "A Planar Germanium Thermophotovoltaic Energy Converter", S. M. Thesis, Department of Electrical Engineering, September 1967.

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

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

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

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

P. S. Showman, "Limitations on the Offset Voltage of Integrated DC Amplifiers", S. M. Thesis, Department of Electrical Engineering, September 1967.

S. M. Spitzer, "Second Breakdown and Thermal Instabilities in Transistors", S. M. Thesis, Department of Electrical Engineering, June 1967.

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

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

T. E. Sharon, "A Technique for Electroreflectance Measurement", S. B. Thesis, Department of Electrical Engineering, February 1967.

Publications

G. C. Ebner and P. E. Gray, "Static V-I Relationships in Transistors at High In ction Levels", IEEE Trans. on Electron Devices, ED-13, October 1966, 692-700.

B. D. Wedlock, et. al., "Investigation of a p-i-n Structure Germanium Photovoltaic Cell", Technical Report ECOM 01978-2, June 1967.

B. D. Wedlock and R. Siegel, "Investigation of a p-i-n Germanium Device for Thermophotovoltaic Conversion", Proc. 20th Annual Power Sources Conference, pp. 182-186, October 1966.

S. D. Senturia, A. C. Smith, and P. L. Sagalyn, "Carrier-Dependent Pb^{207} NMR Shifts in n-type and p-type PbTe", paper presented at American Physical Society Meeting, Washington, D. C., April 27, 1967. Abstract published in Bull. Am. Phys. Soc., 12, 574 (1967).

G. S. Almasi, Scientific Report No. 2, Contract: NASA Grant NsG 496 (part)MIT Task 76153 (identical to Ph. D. Thesis).

A. W. Carlson, Scientific Report No. 3, Contract: NASA Grant NsG 496 (part) MIT Task: 76153 (identical to Ph. D. Thesis).

G. S. Almasi and A. C. Smith, "CdTe-HgTe Heterostructures", J. Appl. Phys., (accepted for publication).

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MICROWAVE AND QUANTUM MAGNETICS GROUP

Personnel

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* A. Platzker, Research Assistant, Electrical Engineering
S. Rezende, Research Assistant, Electrical Engineering
* L. Tocci, Research Assistant, Electrical Engineering
J. Doane, Graduate Student, Electrical Engineering
W. J. Ince, Graduate Student, Electrical Engineering
E. Venturini, Graduate Student, Electrical Engineering
M. Zahn, Graduate Student, Electrical Engineering
Barbara Baldassarre, Secretary, Electrical Engineering

Personnel who have left during the period

Professor T. S. Chang, (Visiting Associate Professor, Electrical Engineering)(Now with Northrop Space Laboratories, Huntsville, Alabama)
Dr. P. H. Cole (Now Senior Lecturer in Electrical Engineering at the University of Adelaide, Adelaide, Australia)
Dr. P. O. Henk, Research Associate (Visiting), Electrical Engineering, (Returned to the Laboratory for Electronic Engineering Materials, DTH, Lyngby, Denmark)
Dr. C. P. Hartwig, (Now with the Raytheon Research Division, Waltham, Massachusetts)
Dr. M. A. Wanas, DSR Staff, Electrical Engineering, (Now at Assiut

University, Assiut, Egypt)
R. A. Williams (Now with Fairchild Semiconductor, San Francisco, Cal.)

Degrees Granted

A. Platzker, S.M., Electrical Engineering, January 1967
H. L. Hu, S.M., Electrical Engineering, June 1967
R. A. Williams, S.M., Electrical Engineering, September 1967
D. Bullock, S.M., Electrical Engineering, September 1967
L. Tocci, E.E., Electrical Engineering, September 1967
L. Kammerdiner, S.B., Electrical Engineering, September 1967

Sponsorship

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

Research Report

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

make possible novel microwave devices such as magnetoelastic wave parametric amplifiers, tunable delay lines and pulse compression filters.

1.0 Magnetic Losses

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

1.1 Resonance Losses in Garnets

Measurements of the resonance linewidth in silicon doped yttrium-iron garnet (YIG) have been made at 13.5 GHz between room temperature and the Curie point. The linewidth shows a pronounced peak at 105°C. The anisotropy of the peak, measured in the (110) plane, can be explained in terms of the 4-level valence-exchange model proposed by Clogston. The numerical value for the electron ordering energy extracted from the analysis of the microwave data agrees very closely with what Hunt obtained from his magnetic anneal investigation carried out previously in our laboratory. From the temperature dependence of the linewidth we calculate that the activation energy for electron hopping is 0.25 ev, a value quite close to that found in our conductivity measurements. These resonance studies, which are being made by L. Tocci, will be extended to additional frequencies and to a variety of sample compositions.

The effect of the valence-exchange mechanism on the effective anisotropy fields in Si-YIG is being studied by D. Bullock.

2.0 Magnetic Domains

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

2.1 Domain Wall Motion in Garnets

Our initial studies of domain-wall switching velocity in single crystals of YIG focussed on the role of Fe^{2+} as a "relaxer" ion. Recently, we have studied wall switching as a function of temperature in picture-frame crystals of YIG doped with erbium. The wall mobility results for

Er-YIG are quite similar to those for Fe^{2+}-YIG. This similarity confirms a previous conclusion, reached on the basis of other evidence, that the switching velocities observed in Fe^{2+}-YIG are not controlled by the valence-exchange mechanism.

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

2.2 Observation of Domain Patterns

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

3.0 Magnetoelastic Studies of Magnetic Crystals

Personnel: Professor F. R. Morgenthaler; A. Platzker

The temperature regulator and new sample holder for the ultrasonic spectrometer have been completed and used to measure the temperature dependence of the first order magnetoelastic and second order elastic constants for single crystal YIG. The measurements were made in the range 80-295^{o}K and temperature stabilization was achieved to within 20 mdeg. This work is described in detail in the S.M. thesis of Mr. A. Platzker.

4.0 Frequency and Mode Conversion of Velocity Modulated Magnetoelastic Waves

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

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.

A detailed analysis of the propagation of magnetoelastic waves in spatially uniform, time varying magnetic fields has been carried out, using small signal momentum conservation and coupled mode theory. The magnon/phonon conversion efficiencies have been obtained in terms of critical time gradients of the field. The latter were derived for both shear and longitudinal magnetoelastic waves propagating along principal crystallographic directions. The analysis reveals that for field gradients much less than the critical values, negligible momentum is exchanged between the different branches of the magnetoelastic dispersion relation. In this case, and as expected, propagation occurs with constant wavenumber and momentum, and variable frequency, group velocity, power flow, and pulse duration. Experimental confirmation of these effects in axially magnetized YIG rods has been obtained for the cases when the injected signal is either a magnon (fine wire excitation) or a phonon (piesoelectric excitation). Pulse compression or expansion and change in echo delay time caused by the group-velocity modulation were observed as well. Earlier experimental work involved pulsed frequency conversion of magnetostatic spin waves in an axially magnetized <100> YIG rod in which both upward and downward shifts of from 20-900 MHz were achieved. All of this work will be described in detail in the Ph. D. thesis of S. Rezende.

5.0 Phonon-Pumped Magnon Instabilities

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

5.1 Phonon-Pumped Magnons in Ga-YIG

The construction of a phonon-pump spectrometer for operation in the frequency range 0.95 - 1.5 GHz. has been completed. The system has been operated in the linear regime over a 400 MHz frequency band centered at 1.2 GHz. In the phonon induced parallel pump instability there are a number of possible spin wave pairs that satisfy the energy and momentum conditions. In order to decide which pair gives the lowest threshold it is necessary to know how the spin wave linewidth varies with wave number. Photon parallel-pump experiments have been performed at 9.17 GHz and 4.2 GHz. In all cases the spin wave linewidth was given by an equation of the form $\Delta H_k = \Delta H_{k\to 0} + Bk$ for values of k below the 3-magnon interaction.

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

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

5.2 Phonon-Pumped Magnons in an Antiferromagnet

Theoretical studies of phonon-pumped magnons in "flopped" uniaxial antiferromagnets are being extended to the cubic antiferromagnet $RbMnF_3$. Preliminary results indicate that the thresholds will be in accord with earlier estimates.

6.0 Magnetic and Elastic Studies of the Antiferromagnet $RbMnF_3$

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

6.1 Coupled Electronic and Nuclear Modes

As preparation for an experimental study of the coupled electronic and nuclear resonance modes in $RbMnF_3$, W. J. Ince has completed a preliminary theoretical investigation of the associated mode spectra. This has served as a basis for planning the experimental program which will include double resonance studies.

6.2 Nonlinear Effects in Antiferromagnetic Resonance

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

The interpretation of these experiments in terms of a variety of models has been investigated. The existing analyses for the instability threshold, which do not apply to the common experimental situations, were extended to include an arbitrary form of anisotropy surface in the flopped configuration. The experimental results, which include measurements of low power resonance linewidth and high power instability threshold, show the uniform sample concept to be clearly inadequate. An alternative but unsophisticated theory which assumes the sample to be composed of uncoupled regions of varying characteristics can be made to fit the observations by a suitable adjustment of material parameters. A more refined version of this theory, which assumes a random variation of anisotropy field (possibly of strain origin as suggested by Eastman) with a certain autocorrelation distance has been prepared. When the autocorrelation distance exceeds a certain quite small value, some simplifications in the theory are possible and permit a simple comparison with experiment. The experiments have been interpreted successfully along these lines. It is interesting to note that the magnitude of the autocorrelation distance is not provided by experiments of this nature. Possibly

experiments involving optical scattering from antiferromagnetic magnons can be carried out and may allow determination of this distance. A second set of nonlinear phenomena used for studies of this material are those which connect harmonically related modes of resonance that exist in certain situations in cubic antiferromagnets when the easy axis lies along the body diagonals. The details of this research are described in Microwave and Quantum Magnetics Group Technical Report 9.

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

Personnel: Professor F. R. Morgenthaler

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

Small signal equations of motion governing the elastic displacement and sublattice magnetization vectors in a magnetoelastic ferrimagnet were used to formulate conservation laws that allow identification of the small signal power, energy, stress, and momentum. These quantities include contributions from the electromagnetic, Zeeman, exchange, anisotropy, elastic, and magnetoelastic fields. Both time-dependent and complex forms of the power theorem have been derived and a time-and space-dependent stress-momentum theorem given for a medium with spatially uniform equilibrium parameters. The small signal torque density and power flow vectors were used to deduce self-consistent boundary conditions that connect the values of the small signal fields on the two sides of a surface of passive discontinuity. These results were in turn employed to generalize the stress tensor so that its components remain finite in a medium with spatially nonuniform equilibrium parameters. In this case, nonconservation of stress-momentum occurs and leads to the existence of a nonzero small signal force density. The general time- and space-dependent equations were also used to derive approximate equations of motion governing localized wave packets described

in terms of quasiparticles. The results have been specialized to the cases of a ferromagnet and an antiferromagnet. On the basis of the work, calculations of magnon trajectories are being carried out for both the microwave and exchange bands. Exchange-band magnons are of interest because with respect to the microwave branch magnons their effective mass is of the opposite sign.

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

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

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

Theses

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

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

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

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

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

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

Publications

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

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

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

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

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

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

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

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

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

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

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

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

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

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CRYSTAL PHYSICS LABORATORY

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R. L. Curtis, Research Assistant (Now at Instrumentation Laboratory, MIT)
A. L. Harmer, Research Assistant (Now Graduate Student at Oxford University, England)
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Degrees Granted

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

Sponsorship

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

1.0 Chemical Preparation of Feed Material

Personnel: Dr. D. Gabbe; K. Bangerskis

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

1.1 Preparation of Cuprous Halides

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

1.2 Preparation of Fluorides

Techniques have been developed for the chemical purification of rare earth fluorides, YF_3, $LiYF_4$, and other fluorides. High-temperature hydrofluorination is used as the final step at present, but work is continuing on high-temperature zone-refining. A temperature controller has been added to the high-temperature zone refiner, and work has concentrated on trying to eliminate contamination from the boat and susceptor materials.

Since both tantalum and molybdenum appear to contribute to the contamination, the use of graphite foil shielding and graphite boats is currently being studied.

1.3 Preparation of Thallium Tungstate ($TlWO_4$)

This compound was precipitated from equimolar $TlNO_3$ and Na_2WO_4 aqueous solution as a fine powder. Digestion at 90°C overnight yielded hexagonal plates fo the compound $T._2WO_4$. Some decomposition of the material occurs below its melting point, so this work was not pursued.

2.0 Crystal Growth

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

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

2.1 Growth from Aqueous Solution

2.1.1 Potassium Nitrate (KNO_3)

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

2.2 High-Temperature Solution Growth

2.2.1 Ferroelectric Crystals

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

2.2.2 Complex Germanates

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

2.2.3 Garnets

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

2.3 Growth from the Melt

2.3.1 Lithium Yttrium Fluoride ($LiYF_4$)

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

2.3.2 Rubidium Manganese Fluoride ($RbMnF_3$)

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

2.3.3 Calcium Tungstate ($CaWO_4$) and other Scheelites

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

2.3.4 Growth by Flame Fusion

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

3.0 Crystal Properties

Personnel: Professor A. Smakula; Drs. A. Linz, R. Mykolajewycz,

J. Kalnajs; E. Farrell, F. Lay; T. Davis, A. Harmer; A. Vetrovs

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

3.1 High-precision Lattice Constant and Density Determination

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

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

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

3.2 Thermal Expansion Coefficient

Thermal expansion coefficient measurements are used for the characterization of crystals, particularly in connection with anharmonicity

and polarization effects. It would be very desirable to extend such measurements over a wide temperature range. Unfortunately at the present time the measurements are restricted to the range close to room temperature. The expansion coefficients of CuCl and CuBr have been determined by density measurements. The values obtained are:

$$\text{CuCl},\ t = 20 - 30^{\circ}\text{C},\ \alpha = 13.6 \times 10^{-6}/^{\circ}\text{C}$$
$$\text{CuBr},\ t = 20 - 30^{\circ}\text{C},\ \alpha = 15.1 \times 10^{-6}/^{\circ}\text{C}$$

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

3.3 Microhardness of Mixed Crystals

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

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

The microhardness of single crystals depends also on the orientation of the indenter with respect to the crystal orientation. In alkali halides with NaCl structure the greatest hardness on the cubic face

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

3.4 Optical Properties

3.4.1 Optical Absorption of Single Crystals

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

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

The ultraviolet and infrared absorption edges of highly purified copper halides have been determined. The CuCl transmits from 0.4 to 20μ and the CuBr from 0.435 to 30μ. The ultraviolet and infrared absorption of $RbMnF_3$ has been measured at 77 and 300°K. There are three strong and four weak bands in the ultraviolet and two weak ones in the visible. Most of the bands split at low temperature. In the infrared $RbMnF_3$ is transparent up to 12μ.

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

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

3.4.2 Absorption Spectra of Hydrogen and Deuterium in $KTaO_3$

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

3.4.3 Optical Absorption Spectra of Minerals

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

These include the minerals cordierite and tourmaline, which occur naturally and have a variety of elements such as Fe^{+2}, Fe^{+3}, and Mn^{+2} as doping agents. Studies of both these materials have been completed in detail. The principal coloring agent has been found to be Fe^{+2} in distorted octahedral symmetry sties. In cordierite this gives rise to a blue color, while in tourmaline the color variations range from pink due to Mn^{+2}, to green, blue and black due to Fe^{+2}. A brown variety also occurs due to a high amount of Fe^{+3}. Synthetic tourmaline with the proper amount of Fe^{+3}/Fe^{+2} doping, cut in the proper direction, may well produce second harmonic generation for a variety of laser frequencies currently available, while the weak field provided by the open channels in cordierite may be an excellent site for rare earth elements.

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

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

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

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

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

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

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

3.4.6 Temperature-dependent Fluorescent Emission in $RbMnF_3$

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

4.0 Low Temperature Ferroelectric Transitions

Personnel: T. G. Davis

Sponsorship: Advanced Research Projects Agency

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

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

5.0 Dielectric Properties of Crystals

Personnel: R. Mykolajewycz

Sponsorship: Air Force Cambridge Research Laboratories

5.1 Dielectric Constant and Loss of LiF at Low Temperature

Using the variational method of Slater and Kirkwood and adopting Landshoff's method for evaluation of the exchange integrals among the non-orthogonal wave functions, Yamashita computed the dielectric constant of LiF for $0^{o}K$, $\varkappa_0' = 10.1$. This value was compared with the room temperature value of 9.3. The dielectric constant of LiF at low temperature was not known. We measured the dielectric constant of LiF with frequencies 10^2 - 10^7 cps and in the temperature range from $-195^{0}C$ to $+500^{o}C$. As with NaCl, the dielectric constant of LiF increases with temperature in the whole temperature range. At $25^{o}C$ it has a value of 9.1 and at $-195^{o}C$ a value of 8.45. The extrapolated value to $0^{o}K$ is 8.4. The discrepancy between the experimental and theoretical value is 20%.

5.2 Dielectric Constant of CuCl and CuBr

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

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

Theses

F. Martino, "Eigenstates of Deep Trap Impurities: The F Center in KCl." Ph.D. Theses, September 1966.

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

B. Chen, "Electrical Investigation of Doped Potassium Tantalate Crystals", B.S. Thesis, February 1967.

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

Publications

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

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

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

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

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

METALLURGY

PHYSICS OF SOLIDS

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Degrees Granted

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

Sponsorship

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

Introduction

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

The general areas of research interest are the scattering of electrons, neutrons, and x-rays from solids and liquids; the electronic structure of metals, alloys, and molecules; order-disorder phenomena;

ultrasonic properties of solids; and the study of local environments in solids. Research programs in these areas are described in detail in the following sections.

1.0 Spin Correlations in Magnetic Materials

Sponsorship: National Science Foundation

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

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

2.0 Atomic Arrangements in Selenium

Sponsorship: Xerox Corporation

A study is being made of the structure of vitreous and crystalline selenium. X-ray diffraction data at 25 and -196°C have been used to obtain radial distribution functions for amorphous and hexagonal selenium. The amorphous selenium exhibits strong correlation peaks at 2.43, 3.75, 5.8, 7.2 and 9.3 A. The first two distances are observed in both the hexagonal form, which consists of spiral chains, and the monoclinic form, which consists of eight-membered puckered rings. The remaining major

peaks do not correspond to intramolecular distances in any of the crystalline forms. Attempts have been made to match the experimental amorphous distribution function with models which involve perturbations of the atom positions in the hexagonal and in the monoclinic crystalline forms. A computer array consisting of 100 atom positions is used and perturbations are chosen by a Monte Carlo procedure which allows only those perturbations which improve the fit to the experimental distribution function. It has been shown that relatively small static displacements are sufficient to convert the monoclinic ring structures to the observed vitreous form. Much larger perturbations are required to convert the hexagonal chain structure into a form which provides a suitable amorphous radial distribution function. It is concluded that vitreous selenium at room temperature probably consists mostly of slightly distorted rings along with some atoms whose local symmetry is like that in the chains. Such a structure appears to be consistent with recent infrared and Raman data.

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

3.0 Ultrasonics at Phase Transitions

Sponsorship: Advanced Research Projects Agency

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

(a) The critical point where critical-like behavior is observed in both the compressibility and attenuation.
(b) Below the critical temperature where the frequency dependence of the attenuation indicates the possible influence of domain walls.

The results are currently being analyzed.

4.0 Theoretical Electronic Structure of Materials

Sponsorship: Advanced Research Projects Agency

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

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

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

(c) The calculation of the one-electron eigenstates associated with polyatomic molecules and macromolecules of biological interest. A Green's

function technique has been developed for the approximate determination of the electronic structures of complex molecular systems. The computational simplicity and applicability fo this method to molecules of arbitrary sterochemical structure are dependent on the adoption of a model Hartree-Fock Hamiltonian similar to that used in energy-band calculations for crystals. The method is of particular advantage in treating large polyatomic systems where more conventional molecular-orbital techniques are difficult to apply. Projected applications include molecular complexes such as the sulfate ion and the metal porphyrins, which are significant to biology. The method can also be applied to determinations of both the localized electronic structure and the energy bands of periodic, quasi-periodic and aperiodic macromolecular systems; e.g., molecular crystals, polymers, and helical systems important to biology (proteins, DNA, etc.).

5.0 Fermi Surfaces of Ordered Alloys

Sponsorship: Advanced Research Projects Agency

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

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

into account.

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

(c) AuSn (NiAs structure). High-field magnetoresistance measurements indicate that the Fermi surface of AuSn supports open orbits in [0001], $<10\bar{1}0>$, and $<11\bar{2}0>$ directions. Cross-sectional areas of the Fermi surface have been measured with the Shubnikov-de Haas effect but the amplitude of the oscillations is large enough to be observed only when the field is in the basal plane. Three sets of frequencies were observed and the results are being compared with the single-OPW Fermi surface model.

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

6.0 Electronic Structure of Dilute Alloys

Sponsorship: Advanced Research Projects Agency

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

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

Sponsorship: U. S. Air Force Wright Air Development Center

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

8.0 Inelastic X-ray Scattering from Beryllium and Beryllium Alloys

Sponsorship: U. S. Air Force Wright Air Development Center

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

The experimental arrangement utilizes a line-focus molybdenum target x-ray tube, with two crossed $\pm$ 3^{o} molybdenum soller slits between the tube focal spot and the specimen. Radiation scattered at a variable angle from the specimen is energy-analyzed using the (400) reflection of a ground and bent LiF crystal analyzer, mounted on the central post of a diffractometer. Data is obtained by rotating the analyzer crystal and detector, in the usual manner, over an angular region sufficient to include the energy range of interest. The data is recorded in a 1024 channel multiscalar, whose channels are commutator-synchronized to the

diffractometer; a complete data set represents many successive passes over the required angular region with fast reversal of the diffractometer and triggering of the multiscalar being controlled automatically. Thus the inherently low counting rates which are commensurate with fine resolution can be utilized without introducing a sensitivity to slow variations of the x-ray supply.

9.0 Low Angle Scattering of X-rays

Sponsorship: Advanced Research Projects Agency

(Research performed in cooperation with Professor J. W. Cahn)

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

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

10.0 Atomic Arrangements in Interstitial Phases

Sponsorship: United States Steel Corporation

(Research performed in cooperation with Professor M. Cohen)

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

(a) The change in elastic properties with oxygen addition; i.e., lattice dynamical effects of interstitial alloying.
(b) The degree of lattice distortion produced by the oxygen interstitials - an x-ray study.

(c) The degree to which the oxygen atoms are in ordered sites within the zirconium lattice - an x-ray study to examine the possibility of an order-disorder transition.

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

11.0 On Line Systems for Numerical Analysis

Sponsorship: Advanced Research Projects Agency, Office of Naval Research (Project MAC)

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

The complete specifications for the new system, even in their initial and tentative form, are far too numerous to list here. It is fairly certain however (a) that the available classes of data entities will be enlarged to include two- and three-dimensional "functions" of specifiable independent variables, as well as three-dimensional arrays; (b) that there will be generalized, multiparameter operators which will be able to appear

directly in the equation format; (c) that the present "command sequence" concept will be broadened to include flexibility regarding the definition of local variables; and (d) that it will be possible to retain the symbolic definition of data entities, perhaps for subsequent symbolic manipulation.

12.0 A Teacher-oriented System for Writing Teaching Programs

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

13.0 Transport Properties and Magnetism in Alloys

Sponsorship: Advanced Research Projects Agency

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

In addition, sample preparation work has begun with the aim of investigating the formation of localized moments in normal metals with

small amounts of magnetic materials added.

Theses

T. A. Rowe, "Atomic Arrangements in Amorphous and Hexagonal Crystalline Selenium", S.M. Thesis, Department of Metallurgy, February 1967.

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

Publications

R. R. Fessler, R. Kaplow, and B. L. Averbach, "Pair Correlations in Liquid and Solid Aluminum", Phys. Rev. 150, 34 (1966).

U. H. Lindborg, and B. L. Averbach, "Crystallographic Aspects of Fracture in Martensite", Acta Met. 14, 1583 (1966).

I. A. Blech, and B. L. Averbach, "Long-Range Magnetic Order in MnO", Phys. Rev. 142 287 (1966).

H. Amar, and K. H. Johnson, "Electronic Structure of IB-IIB Alloys", in Optical Properties and Electronic Structure of Metals and Alloys, edited by F. Abeles (North-Holland Publishing Co., Amsterdam), 586 (1966).

K. H. Johnson, "Relationship Between the Augmented-Plane-Wave and Korringa-Kohn-Rostoker Methods of Band Theory", Phys. Rev. 150, 429 (1966).

K. H. Johnson, "Multiple-Scattering Model for Polyatomic Molecules", J. Chem. Phys. 45, 3085 (1966).

B. Golding, S. C. Moss, and B. L. Averbach, "Composition and Pressure Dependence of the Elastic Constants of Gold-Nickel Alloys", Phys. Rev. 158 (1967).

S. L. Strong, and R. Kaplow, "Diffuse Double Diffraction of X-rays", Acta Cryst. 23, 38 (1967).

A. Ruyle, J. Brackett, and R. Kaplow, "The Status of Systems for On-Line Mathematical Analysis", Proceedings of the Spring Joint Computer Conference (1967).

J. Brackett and R. Kaplow, "X-Y Graph Production and Manipulation", Proceedings DECUS Display Applications Symposium (1967).

D. J. Sellmyer, "Low Temperature Sample Orienting Device with Two Degrees of Freedom", Rev. Sci. Instr. 38, 434 (1967).

D. J. Sellmyer, J. Ahn, and J. P. Jan, "High-Field Magnetoresistance of Ordered Beta Brass", Phys. Rev. 161, 618 (1967).

S. C. Moss, "Local Order in Solid Alloys-I", in Local Atomic Arrangements Studied by X-ray Diffraction, edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach Science Publishers, Inc., New York), (1967).

H. Amar, K. H. Johnson, and C. B. Sommers, "Electronic Structure of Alpha Brass", Phys. Rev. 153, 655 (1967).

B. Golding and S. C. Moss, "A Re-calculation of the Gold-Nickel Spinodal", Acta Met. 15, 1239 (1967).

Papers Accepted for Publication

J. E. Woodilla and B. L. Averbach, "Modulated Structures in Au-Ni Alloys", Acta Met. (in print).

S. C. Moss, "Local Atomic Displacement in Iron-Carbon Martensite", Acta Met.

S. C. Moss and B. L. Averbach, "Local Atomic Configurations in a Gold-Nickel Alloy", in Proceedings of Conference on Small Angle Scattering of X-rays, edited by H. Brumberger (Gordon and Breach Science Publishers, Inc., New York), (1967 expected).

K. H. Johnson, "The Energy Bands and Fermi Surfaces of IB-IIB Alloys", in Symposium on the Status of Energy Band Theories for Metals and Alloys, Proceedings of AIME Meeting in Los Angeles, (Gordon and Breach Science Publishers, Inc., New York), (1967).

K. H. Johnson, "Multiple-Scattering (Green's Function) Model for Polyatomic Molecules, Theory II", International Journal of Quantum Chemistry (1967).

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HIGH TEMPERATURE METALLURGY

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P. Bridenbaugh, Research Assistant
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Sponsorship

Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio,
F33615-67-C1441, DSR 70324

National Aeronautics and Space Administration, Washington, D. C., NsG-117-61, DSR 76243
Naval Air Systems Command, Department of the Navy, Washington, D. C., NOOO 19-67-C-0220, DSR 70297
Advanced Research Projects Agency, SD-90, DSR 75121
National Science Foundation, Washington, D. C., GK-1374, DSR 70290
U. S. Army Research Office, Durham, North Carolina, DA 31-124-ARO-D-328, DSR 74613
Office of Naval Research, Department of the Navy, Washington, D. C., Nonr 3963(18), DSR 74621

Research Report

1.0 Dispersion Strengthening

Personnel: Professor N. J. Grant; F. Hunkeler, H. Dalal, W. Schilling, G. Ewell, D. Kenagy

Sponsorship: National Aeronautics and Space Administration, Office of Naval Research

Utilizing dilute Fe-Be alloy powders, Fe-BeO alloys ahve been prepared in extruded bar form. Extrusions were made both in the ferritic and in the austenitic regions. Hardness, tension properties, and stress rupture tests at 650°C. The materials will be studied to determine the role of stored energy of deformation as the probable mechanism of alloy strengthening (Mr. Hunkeler-NASA). The activity of Cr and Cr_2O_3 in oxidation resistant, oxide dispersion strengthened alloys and their effects on the stability of the refractory oxides (BeO and ThO_2) is being determined. At the same time, an effort is being made to produce materials suitable for service above 1100°C for long-time applications (Mr. Dalal-NASA). Cu-Al alloys have been comminuted to submicron flakes to provide powders which can be either surface oxidized or internally oxidized, resulting in a matrix of Cu which is solid solution strengthened by aluminum and dispersion strengthened by Al_2O_3 (Mr. Schilling-NASA). The deformation and

fracture modes of oxide dispersion strengthened alloys are poorly known, expecially for alloys with oxide particles as fine as 50 to 200 Å and with particle spacings as fine as 0.2 micron. Both light and electron microscopy are being utilized to establish the behavior patterns. Where particles are finer than about 0.2 microns, transmission microscopy is being utilized (Mr. Ewell-NASA). Using five types of dispersoids at particle sizes from 0.01 to 25 micron, and at volume contents of 3 to 11 percent, copper-dispersion strengthened alloys are being studied to determine the mechanism of strengthening. (Mr. Kenagy-ONR)

2.0 Deformation and Fracture at Hot Working Temperatures

Personnel: Professor N. J. Grant; P. Bridenbaugh, R. Kane, W. Ioup

Sponsorship: Naval Air Systems Command

Mr. Bridenbaugh has studied both cast and wrought forms of pure Mo and the highly alloyed TZC composition to establish the mechanism of deformation and fracture. Being examined are the roles of strain rate, temperature, structure, and grain size on the resultant ductility at fracture. Efforts to improve hot plasticity by recrystallizing the structure are being made. Mr. Kane has performed similar studies with several grades of pure iron. He has achieved very large improvements in ductility at fracture by straining the cast materials at high strain rates to strains of 10 to 30%, followed by a holding time at temperature to allow grain refinement. A determination of the creep deformation process has been made. Mr. Ioup has established the very important role of grain size, chemical purity and particle cleanliness on the storage of energy of deformation, which leads either to grain growth (poor ductility) or grain refinement (improved ductility).

3.0 Equilibrium and Non-Equilibrium Alloy Phase Studies

Personnel: Professor N. J. Grant; Drs. R. Wang, B. C. Giessen, H. Matyja, J. T. Blucher; C. Jansen

Sponsorship: U. S. Army Research Office-Durham, Advanced Research Projects Agency, National Science Foundation, National Aeronautics and Space Administration

In this program, Dr. Wang is completing an investigation of pseudobinary AB_3 phase alloy systems containing gold and transition metal combinations; many structural analogies in the behavior of gold and the platinum group metals were observed. (ARO-Durham)

Dr. Giessen has participated in a comparative study of the binary alloy systems of gold with rare earths elements; he is continuing an investigation of the alloy chemistry of ordered transition metal alloy phases. (ARO-Durham; ARPA)

Dr. Matyja has completed an electron microscope study of the decomposition of metastable supersaturated Al-Si alloys; he has also participated in a determination of the dendrite size of splat cooled alloys as a function of the cooling rate. (NSF, NASA)

Mrs. Jansen is completing a study of the metastable solid solubilities of Cu, Ni, Co, and Fe in Al, and has initiated an electron microscope study of precipitation from some of these supersaturated solid solutions. Dr. Blucher continues in an effort to produce large quantities of rapidly quenched alloy material by extending the splat cooling process to larger quantities of powders; two atomization techniques have been developed each capable of producing useful powders over a range of quenching rates. (NASA)

Dr. Giessen has continued a study of metastable B-metal alloy systems; the scope is evident from the literature list. These studies have recently been extended to metastable transition metal alloy systems. (NSF, ARPA)

4.0 The Role of Strain Rate and Temperature in Low Strain Rate Fatigue

Personnel: Professor N. J. Grant; Dr. J. T. Blucher; P. Knudsen, K. Erhardt

Sponsorship: Aeronautical Systems Division

Dr. Blucher has extended the low cycle fatigue studies with high purity Al to include much wider range of strain rates (0.7 to 500%/minute) and total strains (.25 to 8%). These tests have permitted the fatigue life to be extended to over 100,000 cycles. The modes of deformation and fracture are being studied within this spectrum of test conditions. Dr. Blucher and Mr. Knudsen have studied the low cycle fatigue behavior of two SAP alloys (Al-Al_2O_3) from 20° to 427°C. The extreme stability of the SAP structure permits an evaluation of strain rate and temperature independent of continuously changing structure. Mr. Erhardt is performing similar studies with a commercial, age-hardening aluminum alloy. 2024-T4, this being a system in which structural changes occur readily above 150°C.

5.0 Aging in Al-Zn-Mg Alloys

Personnel: Professor N. J. Grant; W. F. Smith

Sponsorship: None

Mr. Smith is following precipitation phenomena in the Al-Zn-Mg systems, with particular emphasis on grain boundary depletion of precipitates. The roles of specific alloying elements (Cr, Ag, etc.) and of heat treatment on the depletion are being studied.

6.0 Development of Chromium Base Alloys

Personnel: Professor N. J. Grant; R. Davison

Sponsorship: Fairchild Fellowship

Mr. Davison is attempting to obtain a balance between strengthening (low and high temperature), the recrystallization temperature, the transition temperature for ductile to brittle fracture, and resistance to nitrogen pick-up at high temperatures. Stress has been placed on the important role

of fine carbide dispersions and fine grain size on improving the performance of chromium as a base for useful alloys.

Publications

N. J. Grant, "Dispersion Strengthening" (Chapter). Strengthening Mechanisms, Proc. 12th Sagamore Army Materials Research Conference, Ed. J. J. Burke, N. L. Reed, V. Weiss, Syracuse University Press, 1966.

J. Blucher and N. J. Grant, "Low Strain Rate, High Strain Fatigue of Aluminum as a Function of Temperature", Trans. Met. Soc. AIME, 239, p. 805 (1967).

R. J. Murphy and N. J. Grant, "Titanium Carbide, Dispersion Strengthened Nickel by Internal Carburization", ASM Trans. Quart. 60, No. 1. p. 29, (1967).

B. C. Giessen, M. Morris, and N. J. Grant, "Metastable In-Bi Phases Produced by Rapid Quenching", Trans. Met. Soc. AIME, 239, p. 883 (1967).

A. S. Bufferd, K. M. Zwilsky, J. T. Blucher, and N. J. Grant, "Oxide Dispersion Strengthened Platinum", International Jour. Powder Metallurgy, 3, No. 1, p. 17 (1967).

N. J. Grant, "Oxide Dispersion Strengthened Alloys", Second International Powder Metallurgy Conference, Stary Smokovec, Czechoslovakia, (1966).

A. S. Bufferd and N. J. Grant, "SAP Type Alloys Solid Solution Strengthened With Mg", Trans. ASM, 60, No. 3, p. 305 (1967).

B. C. Giessen, P. N. Dangel, and N. J. Grant, "New Phases in the Vanadium-Iridium System and a Tentative Constitution Diagram", J. Less Comm. Met. 13, p. 62 (1967).

B. C. Giessen and N. J. Grant, "The Crystal Structure of $TaNi_3$ and its Change on Gold Working", Acta Met. 15, p. 871 (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, p. 611 (1967).

B. C. Giessen, "Rapidly Quenched (Splat Cooled) Alloys" (Chapter).

Strengthening Mechanisms Proc. of the 12th Sagamore Army Materials Research Conference, v. 12, Syracuse University Press (1966).

To be published

D. L. Ritter and N. J. Grant, "Modes of Deformation and Fracture of Low Cycle Fatigue of Aluminum as a Function of Temperature", Jour. Institute of Metals.

L. L. J. Chin and N. J. Grant, "Stored Energy in Dispersion Strengthened Alloys", AIME.

H. Matyja, B. C. Giessen, and N. J. Grant, "Dendrite Spacings in Rapdily Quenched Aluminum Alloys", J. Inst. of Metals.

M. Itagaki, B. C. Giessen, and N. J. Grant, "Supersaturation in Rapidly Quenched Al-rich Al-Si Alloys", submitted to ASM.

R. C. Ruhl, B. C. Giessen, M. Cohen, and N. J. Grant, "New Microcrystalline Phases in Nb-Ni and Ta-Ni Alloys", Acta Met.

L. L. J. Chin and N. J. Grant, "Release of Stored Energy in Oxide Dispersion Strengthened Copper", Powder Metallurgy, London.

H. Matyja, B. C. Giessen, and N. J. Grant, "An Electron Microscope Study of the Precipitation of Silicon from Splat-Cooled Al-Si Alloys", submitted to AIME.

B. C. Giessen, U. Wolff, and N. J. Grant, "Metastable Simple Cubic Phases Based on Sb and Bi", AIME.

B. C. Giessen, U. Wolff and N. J. Grant, "The Metastable System Al-Ga and the Atomic Volume of Twelve-Fold Coordinated Gallium", J. Appl. Physics.

V. Sadagopan, B. C. Giessen, and N. J. Grant, "Crystal Chemistry of Gold-rich Alloy Phases with the Heavy Rare Earths", J. Less Comm. Met.

C. Gautier-Borromee, B. C. Giessen, and N. J. Grant, "Metastable Pb-Sb and Pb-Bi Alloy Phases", J. Chem. Phys.

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Degrees Granted

K. Morizane, Sc.D., Metallurgy, January 1967

R. S. Mroczkowski, Sc.D., Metallurgy, June 1967
P. Tick, Sc.D., Metallurgy, June 1967
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Personnel who left during the period

V. Sadagopan, Research Associate (Now at AVCO, Everett, Massachusetts)
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Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75122, 75126, 78896
Lincoln Laboratory AF 19(628)-5167(part)
National Aeronautics and Space Administration, NGR22-009-125, DSR 76335
National Aeronautics and Space Administration, NsG-496, DSR 76188
National Science Foundation GK-1653, DSR 70399
Office of Naval Research, Nonr 3963(05), DSR 79450
U. S. Atomic Energy Commission, AT(30-1)-3208, DSR 79878

Research Report

1.0 Compound Semiconductor Surfaces

Personnel: Professors H. C. Gatos, A. F. Witt; C. L. Balestra, T. M. Valahas

Sponsorship: Office of Naval Research and Advanced Research Projects Agency

Our research on the characterization of compound semiconductor surfaces this year was centered on GaAs and CdS.

Sinusoidal and pulsed field-effect experiments have been performed

on etched A and B surfaces of n-type GaAs under various environmental conditions. The problem of electrical contacts on this material has been successfully solved by "sand blasting" the surfaces and by using In dots as solder at 500°C. In an alternative method we obtained satisfactory contacts by using tin and hydrazine monobromide as flux on freshly etched surfaces at 232°C.

In a large number of experiments we studied the dynamic behavior of surface states. The time constant of a surface state was determined from oscilloscope traces in the temperature range from 77°K to 430°K. The experiments were performed under a reduced pressure of $\sim 2 \times 10^{-5}$ torr in air and in an 0_3 environment at atmosphere pressure. From the measured time constants for the transition of electrons from the surface state to the conduction band we could determine the position of a surface state (E_c-E_t) with 0.51 eV. Under our experimental conditions no influence of the ambiant atmosphere on the time constant could be observed.

The investigation of the stationary behavior of surface states, (AC field effect) in the frequency range from 0.01 to 10 cps is currently being pursued.

Work on the characterization of CdS surfaces has been initiated. These experiments are performed in an ultra-high vacuum system under reduced pressures (minimum pressure obtainable 6×10^{-12} torr). The vacuum system used is equipped with a mass spectrometer and automatic pressure control which by means of a back feeding circuit permits complete environmental control at any desired pressure and composition.

For the investigation of CdS surface characteristics we have developed a pressure decay calibration system. A special specimen holder permitting circulation of liquid nitrogen for low temperature work was designed and constructed. For investigations at elevated temperatures the specimen holder is heated by electron bombardment from an electron beam gun.

Initial experiments show that indium, the conventional contact material used on CdS is unsuitable because of excessive surface diffusion at the temperatures at which field effect experiments are performed. Indium has therefore been replaced by vapor deposited silver as contact material. Most recently pulsed field effect experiments were made on

CdS wafers of 0.1 mm thickness. The measured room temperature time constant of the field effect decay was observed to be 10 milliseconds.

2.0 Crystallochemical Approach to Electronic Materials

Personnel: Professors H. C. Gatos, A. F. Witt; V. Sadagopan, P. Bellin, Daryl Carnam, N. Platakis, O. Sandven

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

Our crystallochemical approach, previously described, has been put to further use in correlating and developing new superconductors and semiconductors.

2.1 Superconductors

The critical current as a function of magnetic field has been experimentally determined for 40 representative compositions of the Ti-Nb-V ternary system. Fields up to 120 kilogauss were employed. The wire samples had been severely cold worked. This work complements the transition temperature measurements previously obtained on these samples. T_c was observe l to vary in a manner similar to H_c. The density of states as reflected by the electron to atom ratio appears as the dominant theoretical parameter. Resistivity data at 4.2°K and room temperature has been obtained. It is hoped that these measurements will indicate how the Bardeen-Cooper-Slichter interaction parameter varies with composition. The spread of critical current data indicates that current carrying capacity is extremely sensitive to impurities.

Critical currents (J_c) as high as 4×10^3 A/cm^2 at 80 Kgauss were observed. A current program of heat treatment will result in substantial increases in J_c. This will determine the suitability of these alloys as superconducting magnet materials.

Calculations of the specific heat parameter, γ, have been made using the Ginzburg Landau theory for type II superconductors.

Hardness measurements are being made to further characterize the system.

The current carrying capacity is thought to be related to the dislocation structure. Electron microscopy will be used to investigate this possibility.

A comparative study of the relationships between superconductivity and electronic structure in the transition metal carbides has been undertaken from an experimental and theoretical point of view. Electronic properties which relate to the energy band structure have been chosen to give information about the bonding in these materials, and to gain an understanding of the occurrence of superconductivity in some of the carbides, and to obtain parameters (T_c, N(0), θ_D) which relate to a recently proposed two-band model of superconductivity for the transition metals and their alloys.

Specific heat measurements are being made in the range of temperature from 1-10^{o}K using a continuous warming method, in which heat is added to the sample at a constant known rate, and the subsequent rate of temperature increase is measured. The heat capacity is then obtained as

$$C = P/(dT/dt)$$

where P is the rate of heat input to the specimen, and dT/dt is the time rate of temperature increase. Using the continuous warming method it is possible to obtain high precision data in a relatively rapid manner.

Specific heat measurements have been made on the following systems: TiC (single crystal), TiC, ZrC, HfC, VC, TaC, MoC and WC.

2.2 Semiconductors

The work on vitreous semiconductors is being continued with the systems $xAs_2Se_3 \cdot ySb_2Se_3$. The compounds are synthesized from the elements under vacuum and kept at a temperature of 750^{o}C for 24 hours. The resulting compounds have been analyzed by x-ray diffraction and were identified as glasses. The investigation of the temperature dependence of the resistivity revealed resistivity changes by a factor of 10^7 for the temperature range from 23^{o}C to 300^{o}C. The resistivity was observed to

decrease by a factor of ~ 3 for each 10% increase in Sb_2Se_3 in the system.

3.0 Distribution of Impurities in Solids

Personnel: Professors H. C. Gatos, A. F. Witt; L. Kimerling, R. Singh, D. Miller, L. Golovin

Sponsorship: Advanced Research Projects Agency, National Science Foundation, and the U. S. Atomic Energy Commission

Our investigation of semiconductor crystal growth characteristics and the distribution and incorporation of impurities is being continued. The recently developed technique for the measurement of instantaneous, microscopic rates of crystal growth by means of "rate striations" revealed that during Czochralski growth of semiconductor single crystals the actual rate of growth varies continuously and differs in some instances by order of magnitude from the pulling rate. It was found that the facet growth rate during rotational pulling is numerically identical with the pulling rate but the growth rate in the off-core region is subjected to continuous fluctuations the magnitude of which is determined by the extent of thermal asymmetry in the system, by the temperature gradient in the melt, by the rate of rotation and the rate of pulling.

An investigation of the effects of seed rotation on the uniformity of impurity incorporation revealed that at constant pulling rate the extent of back melting increases with increasing rotational rates up to about 40 rpm. Further increases of the rotational rate lead to a reduction of back melting because of homogenization of the thermal conditions in the melt. However rotational striations which reflect severe heterogeneities in impurity distribution are clearly visible at rotational rates up to 150 rpm. It is observed that crucible rotation is much more effective in eliminating non-rotational impurity striations and results in a better homogeneity of the impurity distribution.

In a series of experiments we investigated the extent of facet formation in InSb from a <111> direction. It was found contradictory to previous literature reports that it is uneffected by the presence of

impurities. The extent of facet formation could, however, be controlled by the temperature gradient across the growing crystal and across the melt. It was also observed that the dislocation density is greatly influenced by the same temperature gradients.

An investigation of the effects of radiation damage on the electrical properties of germanium has recently been initiated. In the first part of this investigation antimony doped single crystal of germanium with low dislocation densities were grown by the Czochralski method. Small samples of this material were subsequently exposed to Co-60 γ-radiation in the irradiation facility of the Massachusetts General Hospital. The preliminary experiments indicate partial compensation due to the presence of radiation induced traps. An apparatus for the measurement of the minority carrier lifetime has recently been constructed. A setup for photoconductivity measurements is currently under construction. The above tools combined with Hall measurements and x-ray analyses will permit a detailed study of the behavior of carriers in the doped and irradiated material.

4.0 Semiconductor Growth

Personnel: Professors H. C. Gatos, A. F. Witt; M. Lichtensteiger, J. M. Harris, G. Galyon

Sponsorship: Advanced Research Projects Agency

Single crystal (111) beta silicon carbide has been grown expitaxially on (111) silicon substrates at 1150°C using a mixture of silane and propane and hydrogen. The quality of the films as revealed by x-ray analysis is good. The thin film single crystals exhibit, however, considerable variation in thickness which is attribtued to unfavorable gas flow conditions. Preliminary experiments indicate the simultaneous deposition of alpha and beta silicon carbide under conditions of increased growth rate. The deposition of SiC on to SiC substrates is being delayed because of the unavailability of a suitable susceptor material. At present experiments are carried out with Ti, TiC, and SiC as prospective susceptors.

The epitaxial deposition of PbSe by sputtering on to glass and sodium chloride substrate has been successful. X-ray analysis indicated single crystalline deposits of <111> orientation on both substrates. It was observed that p- and n-type PbSe can be obtained by varying the substrate temperature. The formation of p-n junctions in PbSe by this method is currently under investigation.

An investigation of the formation of III-V compound alloys in single crystal form has been initiated. Preliminary experiments were carried out with GaSb-InSb in a Czochralski system. Currently under construction is a setup by which Bridgman experiments can be carried out at elevated pressures (10 Kbar).

5.0 High Pressure Studies

Personnel: Professor H. C. Gatos; H. I. Andrews, G. Galyon

Sponsorship: Lincoln Laboratory

Progress continues on the phase relations and polymorphic transformations in the HgSe-HgS system.

Recent work in a liquid pressure-transmitting medium with manganin coil pressure gauge in situ has provided the most accurate data yet on the pressure of the zinc blend cinnabar transformation. A smooth and gradual decrease of transformation pressure as HgS content of the solid solution increases occurs up to at least 50% HgS by weight. HgSe transforms at 7.4 kilobars; the 50:50 alloy transforms at 3.4 kilobars. Similar measurements at temperatures of 125°C and 250°C show increased transformation pressures at all compositions with nearly parallel smooth and gradual decreases as HgS content increases. Further measurements to both higher compositions (approximately 60 weight percent HgS) and to higher temperature (about 400°C) are in progress.

In a solid pressure-transmitting medium, differential thermal analysis is yielding better data on the cinnabar to zinc blend transformation on heating at constant pressure at the mercury sulphide end of the

diagram. The solid medium with its less well defined pressures must be employed because of the higher temperatures required for the transformation and the high pressures required to prevent decomposition of mercury sulphide rich alloys. Experiments using this technique are planned also for determination of melting points across the entire diagram.

The high pressure of cinnabar phase of the alloys may be stabilized at one atmosphere by quenching to liquid nitrogen temperature before releasing the applied pressure. The electrical resistance increases several orders on warming through the transformation giving the reverse transformation temperature. Studies of HgSe on slowly warming are complete.

6.0 Magnetic Resonance in Non-Metallic Spinels

Personnel: Professor H. C. Gatos; J. J. Stickler

Sponsorship: Lincoln Laboratory

Microwave resonance studies have been continued on $CoCr_2O_4$ (ferrimagnetic spiral), and additional spin resonance measurements have been made on MnI_2 (flat antiferromagnetic spiral). The spectra observed in powder samples of $CoCr_2O_4$ and single crystal samples of MnI_2 were measured as a function of frequency and temperature.

Neutron diffraction studies have shown that $CoCr_2O_4$ orders in a ferrimagnetic spiral below $31^{\circ}K$ and has a Neel spin configuration between 86° and $96^{\circ}K$. The microwave spectra measured from the Neel temperature of $96^{\circ}K$ to $4.2^{\circ}K$ exhibit a sharp transition at the spiral ordering temperature of $31^{\circ}K$. Between 31° and $96^{\circ}K$, $CoCr_2O_4$ behaves ferrimagnetically with a net magnetization close to compensation. Two resonance modes were observed in this region, one identified as an exchange mode and the other as a uniform precession mode. The zero-field frequencies and effective g-factors for these modes were computed as a function of temperature using the molecular field calculations of Menyuk and Dwight. Excellent agreement with measured data was obtained. Computer

calculations are now under way to calculate the frequencies of the correlated spiral modes corresponding to the resonance modes observed below 31°K.

Antiferromagnetic resonance has been observed in single crystals of MnI_2 at liquid helium temperatures and in the range of frequencies from 35 to 70 GHz. Neutron diffraction studies have shown that the Mn^{2+} spins order in flat spiral spin configuration below 3.48°K and with a spin propagation vector along the (307) direction. The resonance data indicates the presence of appreciable short-range ordering at 4.2°K. At the lowest temperature reached by pumping on liquid helium, namely 1.5°K, the sample had a zero-field resonance at 48 GHz. At this temperature the resonance frequency varied almost quadratically with applied fields. Several weaker resonances were also observed at the lower temperatures; the origin of these lines is as yet uncertain. All the resonances exhibit some anisotropy with applied field which could be attributed to demagnetizing effects in the planar sample. A theoretical analysis of the resonance based on a modification of the calculations of Cooper et al is being attempted.

7.0 Niobium Oxide Single Crystals

Personnel: Professor H. C. Gatos; E. R. Pollard

Sponsorship: Lincoln Laboratory

A new technique for the growth of single crystals of high temperature materials has been perfected in conjunction with T. B. Reed of Lincoln Laboratory. The technique employs the well known cold hearth phenomenon of arc melting and as such avoids the problem of crucible contamination. The crystals are pulled in the Czochralski fashion from the resultant molten puddle.

Niobium monoxide single crystals have been grown in this furnace and its electrical properties have been investigated as a function of temperature and composition. The NbO single phase field was found to exist from 0.980 to 1.020±0.002 oxygen to niobium molar ratio. Niobium

monoxide has metallic conductivity, ~5 x 10^4 $(ohm\text{-}xm)^{-1}$ at 300°K, is superconducting around 1.4°K, exhibits a slightly increasing magnetic susceptibility with decreasing temperature and increasing oxygen/niobium ratio. The Seebeck Coefficient and Hall constant indicate that the majority carriers are electrons with an effective carrier concentration (at O/Nb = 1) of about 0.4 electron per NbO molecule. The room temperature specular reflectivity was measured out to 12 eV, and Kramers-Kronig analysis has yielded the real and imaginary parts of the complex dielectric constant. The peaks in the imaginary component were correlated with interband transitions and a parameterized tight binding (Slater-Koster scheme) calculation to yield approximate values for band separations. Magnetoresistance measurements have been carried out at the National Magnet Laboratory in fields up to 150,000 gauss. Niobium monoxide exhibits anisotropic magnetoresistance as well as apparent magnetic breakdown at about 20 kG in the (100) direction. With (100) breakdown, all directions had a quadratic dependence on the magnetic field.

Theses

K. Morizane, "Impurity Distributions in Indium Antimonide Single Crystals", Sc. D. Thesis, Department of Metallurgy, February 1967.

R. S. Mroczkowski, "Metallurgical Aspects of Heterojunctions with Diamond Type Structures", Sc. D. Thesis, Department of Metallurgy, February 1967.

P. A. Tick, "Condensation on Equilibrium Surfaces in Simulated Metal Systems", Sc. D. Thesis, June 1967.

Publications

F. J. Bachner and H. C. Gatos, "Superconductivity Degradation in Beta-Tungsten Structure Compounds - $Nb_3Sn(Cb_3Sn)$ and Nb_3Al", Trans. of the Met. Soc. of AIME 236, 1261 (1966).

H. Huff, S. Kawaji and H. C. Gatos, "Relaxation Phenomena at High

Electric Field on the Surfaces of Indium Antimonide", Surface Science 5, 160 (1966).

H. Huff, S. Kawaji and H. C. Gatos, "Field Effect Measurements on the A and B {111} Surfaces of Indium Antimonide", Surface Science 5, 399 (1966).

S. Kawaji and H. C. Gatos, "The Role of Surface Treatment in the Field Effect Anomaly of n-Type InSb at High Magnetic Fields", Surface Science 6, 362 (1967).

A. F. Witt and H. C. Gatos, "Determination of Microscopic Rates of Growth in Single Crystals", J. Electrochem. Soc. 114, 413 (1967).

F. J. Bachner, J. B. Goodenough and H. C. Gatos, "Superconducting Transition Temperature and Electronic Structure in the Pseudo-binaries Nb_3Al-Nb_3Sn and Nb_3Sn-Nb_3Sb", J. Phys. Chem. Solids, 28, 889 (1967).

S. Kawaji and H. C. Gatos, "Electric Field Effect on the Magneto-resistance of Indium Arsenide Surfaces in High Magnetic Fields", Surface Science 7, 215 (1967).

V. Sadagopan and H. C. Gatos, "Average Heats of Atomization and the IV-VI Compound Semiconductors", Solid-State Electronics 10, 441 (1967).

K. Morizane, A. Witt and H. C. Gatos, "Impurity Distribution in Single Crystals. III. Impurity Heterogeneities in Single Crystals Rotated During Pulling from the Melt", J. Electrochem. Soc. 114, 738 (1967).

A. F. Witt, "Study of Impurity Heterogeneities in InSb by Means of a Permanganate Etchant", J. Electrochem. Soc. 114, 298 (1967).

A. F. Witt and H. C. Gatos, "Microscopic Rates of Growth in Single Crystals Pulled from the Melt: Indium Antimonide", J. Electrochem Soc., in press.

SUPERCONDUCTIVE MATERIALS

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B. P. Strauss, Sc.D., June 1967
M. L. A. MacVicar, Sc.D., September 1967

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75124
National Science Foundation, GK 1075, DSR 76350; GK 1071, DSR 76353
Office of Naval Research, Nonr 3963-16, DSR 74611

1.0 High-Field Solid Solution Superconductivity

Sponsorship: Advanced Research Projects Agency, National Science Foundation

Research Report

1.1 Effect of Cold Work on Superconducting Current Density of a 40 wt.% Nb-Ti Alloy

Plastic deformation is effective in increasing the current density, J_c, of these alloys only when severe (ca. 90% R.A.). The critical field is quite sensitive to deformation in this particular alloy and interstitial oxygen does not improve the J_c of cold-worked alloys. The influence of oxygen on J_c of these wires may be explained by changes in the dislocation and martensite plates configuration with oxygen content.

1.2 Superconductivity and Aging in the Nb-Ti Systems

The response of J_c to aging both cold-worked and recrystallized specimens with various oxygen contents, has been studied in this system. Optimum critical fields are found at roughly the 50 wt.% composition whereas optimum J_c is found in alloys with slightly higher Ti content. Several properties, ω and α, are both effective fluxoid pinners and the operative one is dependent on the composition, included oxygen content, of the alloy.

1.3 Yttrium, Lanthanide and Actinide Series Additions in Nb-Ti Alloys

Much higher J_c values have been obtained by adding small amounts of Y, Gd, or Th to Nb-Ti alloys. These addition agents combine with oxygen during aging of the alloy to form an effective fluxoid dispersion. These alloys have the highest current densities of any alloys we have heretofore processed.

2.0 Superconductivity of the Transition Metals

Sponsorship: National Science Foundation

Research Report

We have found that the resistive critical field anisotropy of Nb wire may be altered by processing, particularly drawing, swaging and annealing. We are presently preparing a torsion experiment to test the hypothesis that such behavior is due to "internal surface" nucleation of superconductivity. The role of oxygen in Nb has also been somewhat clarified. The use of ultra-high vacuum has eliminated many spurious contamination effects, and analysis of the diffusion problem has enabled us to homogenize our materials. Ultrasonic and low angle x-ray scattering experiments are underway to test the clustering model. The vanadium tunneling research is also under way.

3.0 Electron Tunneling and Superconductivity of Niobium

Sponsorship: Office of Naval Research

Research Report

3.1 Tunneling into Nb Single Crystals

We have developed a reliable technique for the measurement of

the energy gap in K-space. The gap for the <110> and <112>, and the average gap are all 3.10 mv. For <100>, the gap is 2.84 mv; for <111>, 3.19 mv, and for <311>, slightly more. The angular resolution is the best of any technique, and energy resolution is limited only by temperature and equipment. Low and high energy structure corresponding to multiple gaps has also been observed.

3.2 Tunneling in Alloys

The above-mentioned technique has been adapted for use on alloys. Initial experiments on 80% Nb-20% Ti have succeeded, but junction quality must be improved, as excess currents are still large.

4.0 Superconducting Composites

Sponsorship: Advanced Research Projects Agency

Research Report

Magnetic measurements have demonstrated the existence of a strong double proximity effect in the copper matrix of various Nb-Cu composites of similar geometry. The primary effect persists up to the resistive transition temperature. The secondary effect persists up to about $3^{o}K$.

Publications

L. Gunther and L. W. Gruenberg, "de Haas-van Alphen Oscillations in the Critical Temperature of Type II Superconductors", Sol. St. Comm. 4, 329 (1966).

H. B. Shukovsky, R. M. Rose, and J. Wulff, "Reply to Comments on 'Low Temperature Electrical Resistivity of Lattice Defects in Deformed Tungsten'", Acta Met 15,391 (1967).

T. H. Courtney and J. Wulff, "Matrix-Limited Fatigue Properties in Fibre Composite Materials", J. Mat. Sci. 1, 383 (1966).

G. Beske, P. Hilsch and J. Wulff, "The Effect of Precipitation on Superconducting Properties of an Al-15% Zn Alloy", Trans. Met. Soc., AIME, 229, 890 (1967).

D. A. Colling, K. M. Ralls, and J. Wulff, "Superconducting Transition Temperature of Solid-Solution Ta-Ti Alloys", J. App. Phys. 37, 4750 (1966).

B. P. Strauss and R. M. Rose, "Proximity Effects in a Fine Composite", Physics Letters 25A, 5 September 1967.

Papers Accepted for Publication

L. C. Skinner II and R. M. Rose, "Improvements in the Floating-Zone Electron Beam Technique for the Group V Refractory Metals", in 2nd Int. Conf. on Electron and Ion Beam Science and Technology.

M. L. A. MacVicar and R. M. Rose, "Measurement of the Anisotropic Energy Gap in Nb Single Crystals", in Proc. Symposium on Physics of Superconducting Devices.

T. H. Courtney and J. Wulff, "Quaternary Solid Solution Superconductors", in Physics Letters.

B. P. Strauss and R. M. Rose, "Superconductivity of a Composite of Fine Nb Wires in Copper", to J. App. Phys.

M. L. A. MacVicar and R. M. Rose, "Superconducting Energy Gap of Thin Films", to App. Phys. Letters.

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PHYSICAL METALLURGY - Phase Transitions in Solids, Morphological Stability, Particle Coarsening, Domain Structure

Personnel

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

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75125
Office of Naval Research, Nonr-1841(35), DSR 77618

Research Report

1.0 Massive Transformation in Beta Brass

A capacitor-discharge pulse-heater has been built which permits heating rates of 10^7 ^{o}C/sec. It is being used to study extremely fast solid state reactions in metallic systems.

The massive β-α transformations in brass take about 10 milliseconds to complete at 500^{o}C. The massive α phase starts at β-grain boundaries and grows into the β grain with a measured growth rate of about 1 cm/sec. The transformation occurs only in the limited range of temperature and composition corresponding to the single-phase α region

of the phase diagram. This simple experimental fact leads to some very important conclusions about the nature of the massive transformation.

2.0 Phase Separation and Crystallization in Glass

The theoretical aspects of liquid-liquid separation in glass both by nucleation and growth and by spinodal decomposition were considered and detailed predictions about kinetics and morphology were made for each mechanism. Experience in silicates and in borosilicate glasses seems to indicate that both mechanisms occur.

Various hypotheses about the effect of the liquid-liquid phase separation upon the subsequent nucleation of crystal are being examined theoretically.

Work is being started to verify ideas experimentally in a suitable chosen glass.

3.0 On the Morphological Stability of Growing Crystals

The Mullins and Sekerka formulation for the morphological stability of a growing particle consists of two terms. The first, pertaining to the diffusion field, results in instability, the second, pertaining to the surface tension contribution, stabilizes the crystal up to radii one order of magnitude greater than the critical nucleus size. This, however, is still a very small size.

In the present program other stabilizing factors are examined with particular reference to real crystals. The results are as follows:

(1) The slightly anisotropic surface tension does not result in a stable particle at any size as long as there is no interface kinetics term.

(2) The interface kinetics term stabilizes the particle until it reaches a size which approximately marks the transition from interface control to diffusion control. This is true regardless of surface tension anisotropy. Of particular interest is the growth of polyhedral crystals which continue to grow as polyhedra until the center of a polygonal face approaches equilibrium conditions. Thereafter the center of the polygon

cannot keep up with the periphery and a hopper morphology is predicated.

4.0 Particle Coarsening

Precipitation structures are subject to gradual particle coarsening during exposure to high temperatures. The theory of this phenomenon is being developed for structures in which there is a great deal of regularity in the size and spacing of the precipitated particles. Such structures are attainable by spinodal decomposition and offer great potential for strengthening purposes over the irregular structures arising from nucleation and growth.

5.0 Antiphase Domain Walls in Ordered Structures

When a disordered alloy orders, the same atomic species can be placed on one of several equivalent sublattices. Thus, if ordering proceeds by growth from several centers a domain pattern of ordered regions out of step with one another is formed. The boundaries between domains are internal surfaces called domain walls. In addition certain dislocations in the disordered structure become bounding curves of domain walls in the ordered structure. The domain wall structure is an important factor in determining properties of the ordered material.

A theoretical study of the topology of the domain structure was undertaken and revealed that initially it must be a highly interconnected structure. The simple domain structures seen by transmission microscopy are well annealed crystals and must be the result of much rearrangement and untangling.

A statistical-mechanical study of the antiphase domain wall in a β-brass structure as a function of composition and temperature has shown that it is possible to obtain results that are thermodynamically self-consistent in that the Gibbs adsorption equation is obeyed. Because the chemical potential changes rapidly through the stoichiometric point, and because adsorption to a domain wall is undoubtedly large, marked composition effects are predicted.

Publications

E. L. Huston, J. W. Cahn, J. E. Hilliard, "Spinodal Decomposition During Continuous Cooling", Acta Met. 14, 1053 (1966).

J. W. Cahn, "The Latter Stages of Spinodal Decomposition and the Beginnings of Particle Coarsening", Acta Met. 14, 1685 (1966).

J. W. Cahn, "The Morphological Stability of Growing Crystals", Crystal Growth (proceedings from the International Conference on Crystal Growth, Boston, 1966), Supplement to J. Chem. and Phys. of Solids Pergamon Press (1967).

J. W. Cahn and R. Kikuchi, "Theory of Domain Walls in Ordered Structures-III", J. Phys. Chem. Solids 27, 1305 (1966).

J. W. Cahn, "Significance of Average Mean Curvature and Its Determination by Quantitative Metallography", Trans. AIME 239, 610 (1967).

MARTENSITIC TRANSFORMATIONS IN IRON-RUTHENIUM ALLOYS

Personnel

* Professor J. F. Breedis, Assistant Professor, Metallurgy and Materials Science

** I. R. Sprung, Graduate Student, Metallurgy and Materials Science

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75128

Research Report

The crystallography, morphology and defect structures of martensite have been investigated in iron-ruthenium alloys containing from 7.5 to 17.0 At. % ruthenium. Depending upon composition, two types of transformation products are observed: body-centered cubic martensite (α') similar to that found in stainless steel occurs in alloys containing up to 11.0 At. % ruthenium, while hexagonal close-packed martensite (ϵ') forms in more concentrated alloys. The orientation relationships between the parent austenite and the α' and ϵ' structures, determined through electron diffraction, are near the Kurdjumov-Sachs and the cobalt-transformation relationships, respectively. While many of the α' crystals are twin-related, the interface plane between such crystals is found to deviate from the expected twinning plane by nearly 17^{o}. This deviation can be explained by cooperative slip on closely spaced planes to produce a displaced interface plane. Observations of defect structures show that the stacking fault energy of austenite is around zero, while this energy is finite in ϵ' where unit dislocations were observed in addition to numerous partial dislocations. Consideration of the variations of the M_s-temperature and the extent of transformation with composition indicates that ϵ', which has a higher M_s-temperature, may assist in the nucleation of α', but otherwise hinders its growth.

DEFORMATION OF IRON ALLOYS

Personnel

* Professor J. F. Breedis, Assistant Professor, Metallurgy and Materials Science
** D. B. Snow, Graduate Student, Metallurgy and Materials Science

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75128

Research Report

The plastic deformation of the hexagonal close-packed ϵ-phase of the iron-ruthenium system, which extends from 80 atomic percent iron to pure ruthenium, is being studied as a function of composition, temperature and strain-rate. The slip and twinning systems are being determined and dislocation substructures quantitatively evaluated through transmission electron microscopy.

Other topics under consideration in this program, which also includes face-centered cubic iron-ruthenium-nickel and iron-chromium-nickel alloys are: (1) the nature of defects in the parent phase resulting from rapid quenching and their influence upon mechanical properties, and (2) the influence of clustered vacancy defects and dislocation structures upon the nucleation of martensitic transformations during subsequent sub-zero cooling.

STRENGTHENING OF TITANIUM ALLOYS

Personnel

* Professor J. F. Breedis, Assistant Professor, Metallurgy and Materials Science

M. K. Koul, Graduate Student, Metallurgy and Materials Science

Sponsorship

Air Force Materials Laboratory, AF33(615)-3866, DSR 76337

Research Report

In conjunction with the study of fatigue behavior, the dependence of strength upon structures developed through plastic deformation and phase transformations is being studied in pure titanium, and in binary titanium alloys which contain aluminum, molybdenum or vanadium. Transmission electron microscopy is used to relate mechanical properties to structures developed through conventional tensile deformation, rolling, shock deformation at applied pressures of 75 and 200 kilobars, precipitation of of omega-phase and martensitic transformation. Preliminary observations indicate that enhanced strengths without drastic loss of ductility can be attained through either shock deformation or controlled precipitation of the omega-phase.

FATIGUE IN TITANIUM ALLOYS

Personnel

* Professor J. F. Breedis, Assistant Professor, Metallurgy and Materials Science

R. Stevenson, Graduate Student, Metallurgy and Materials Science

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75128

Research Report

The fatigue behavior of titanium alloys is being investigated as a function of strain amplitude, temperature and grain size. The alloys included in this study are hexagonal close-packed Ti - 4.5 wt. % Al (disordered), Ti - 9 wt. % Al (short-range order), pure titanium, and body-centered cubic titanium-molybdenum alloys. Defect structures produced during cyclic stressing are being correlated with behavior using transmission electron microscopy. Where possible, single crystals will be used in hope of more clearly resolving the dislocation-defect interactions which determine fatigue behavior.

RADIATION DAMAGE IN SOLIDS

Personnel

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

** J. M. Wells, Research Assistant, Metallurgy and Materials Science

W. Carrasco, Technician, Metallurgy and Materials Science

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75129

Research Report

Electron irradiation of body-centered cubic metals and their dilute interstitial alloys is being performed at 4.2°K. Analysis of the decay of resistivity due to vacancies and interstitials coupled with electron microscopy is expected to elucidate the energetics of defect interactions.

NUCLEATION IN NOZZLES

Personnel

Professor P. G. Hill, Associate Professor, Mechanical Engineering

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

R. Roberts, Research Assistant, Mechanical Engineering

Sponsorship

Office of Naval Research, Nonr 3963(07), DSR 79809

Research Report

A critical test of the theory of homogeneous nucleation in vapors is in progress using the supersonic nozzle. The nucleation of H_2O, CO_2, NH_3, $CHCl_3$, C_6H_5Cl, CH_3OH, C_2H_5OH and C_6H_6 had been studied to date and results indicate that neither of several proposed nucleation theories describe the behavior of all these materials satisfactorily. Experiments are in progress to study the earliest stages of particle coarsening in nozzles by means of light scattering.

CRYSTALLIZATION AND PROPERTIES OF POLYMERS

Personnel

* Professor D. R. Uhlmann, Assistant Professor, Metallurgy and Materials Science

T. J. Brown, Engineering Assistant, Metallurgy and Materials Science

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75127

Research Report

The effect of crystallization conditions on the morphology and properties of crystalline polymers is being investigated. The materials being studied initially are polyethylene and some of the important fiber-forming polymers.

CRYSTALLIZATION AND PROPERTIES OF POLYMERS AT HIGH PRESSURE

Personnel

* Professor D. R. Uhlmann, Assistant Professor, Metallurgy and Materials Science

** R. M. Kimmel, Research Assistant, Mechanical Engineering

T. J. Brown, Engineering Assistant, Metallurgy and Materials Science

Degree Granted

R. M. Kimmel, S.M. and Materials Engineer, Mechanical Engineering, June 1967

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 75127

Research Report

The effect of high pressure on the properties and crystallization behavior of high polymers is presently being investigated. The studies are now being carried out in a Bridgman anvil high pressure device and 200,000 psi gas apparatus, while studies in the near future will utilize a large volume solid-medium press as well.

In studying the densification of glass-forming polymers under high pressure, results with polymethylmethacrylate, polystyrene and polycarbonate have indicated that only slight permanent densification is obtained from high pressure treatment. The densification observed on compression in the glassy state can represent a substantial fraction of the densification obtainable by cooling through the glass transition under pressure.

METALS PROCESSING - Casting and Solidification

Personnel

(All personnel from Department of Metallurgy and Materials Science)

* Professor M. C. Flemings, Associate Professor
T. Z. Kattamis, Research Associate
W. A. Brown, DSR Research Staff
P. R. La France, Technical Instructor
L. K. Bigelow, Research Assistant
W. E. Brower, Research Assistant
A. J. Campagna, Teaching Assistant
J. M. Coughlin, Research Assistant
J. Kaneko, Research Assistant
R. Mehrabian, Teaching Assistant
S. A. Metz, Research Assistant
F. R. Mollard, Research Assistant
M. Myers. Teaching Assistant
A. M. Reti, Research Assistant
S. N. Singh, Research Assistant
D. R. Spencer, Research Assistant
R. W. Strachan, Research Assistant
R. A. L. Troup, Teaching Assistant
J. C. Yarwood, Research Assistant
E. H. Backman, Foreman
** R. A. Berry, Technician
A. Kariotis, Engineering Assistant
A. Barbara Rich, Secretary

Degrees Granted

F. R. Mollard, Sc. D., Metallurgy, February 1967

R. W. Strachan, Ph.D., Metallurgy, February 1967
J. M. Coughlin, S.M., Metallurgy, February 1967
J. Kaneko, Sc.D., Metallurgy, August 1967

Sponsorship

Army Materials Research Agency, DA-19-020-AMC-5443(X), DSR 78824
Army Materials Research Agency, DA-19-020-AMC-2231(X), DSR 79885
Army Materiel Command, DA-36-038-AMC-2943(A), DSR 74963
Office of Naval Research, NONR-3963(09), DSR 79988
Advanced Research Projects Agency, SD-90, DSR 78893
U. S. Steel Grant-in-Aid, DSR 79693
American Foundrymen's Society, DSR 70438
American Iron & Steel Institute, DSR 76379

Research Report

Research is primarily concerned with liquid-solid transformations; a central aim of the research is to gain greater control over structure and properties of materials through control of solidification. Work is currently under way in the following areas.

1.0 Crystal Growth

Sponsorship: Advanced Research Projects Agency

Continuing progress has been made in establishment of the Metal Crystal Growth Facility as part of the Center for Materials Science and Engineering. Crystal growing units installed during the previous fiscal year are now in full operation. Two new power sources have been acquired and a variety of refinements of equipment on hand are under way or have been completed. These include construction of apparatus to permit casting levitation melted alloys in small ingot molds under inert atmosphere or

or vacuum.

Research on crystal growth has included continuation of study of structure of crystals grown in a magnetic field, and study of growth of "composite" crystals. These programs are discussed below.

2.0 Effect of Fluid Flow on Structure; Composite Materials

Sponsorship: Office of Naval Research

Research is continuing on effect of fluid flow on structure of metal single crystals and of unidirectionally solidified eutectics. Convection is inhibited by application of a magnetic field and induced by crossed electric and magnetic fields. Significant improvement in perfection of the eutectic crystals is obtained by inhibiting convection.

In related work, two-phase alloys of non-eutectic composition are being grown under steep temperature gradient at slow rate and it is shown that two-phase "composites" are produced in which the second phase is lamellar or rod-like. These resemble lamellar eutectics but can be grown of compositions far removed from eutectic composition. Initial work has been on lead-tin alloys. Other current work is studying extension of this technique to alloys in systems containing a peritectic.

A new study has been initiated to study effects of extremely strong convection on solidification structures.

3.0 Growth Kinetics and Structure of Metals Solidified at Large Degrees of Undercooling

Sponsorship: Department of the Army, U. S. Steel Corporation

Primary aim of this study is to investigate effects of large degrees of undercooling (up to 300°C.) on structure and solute redistribution in metallic alloys. A secondary aim of the research is to develop improved methods for producing nonequilibirum structures (supersaturated and/or glassy structures) by rapid cooling of metallic melts.

Experimental work is currently on (a) bulk samples (approximately

100 grams) undercooled in glassy containers, and (b) levitated metal droplets. The levitated metal droplets are undercooled and dropped between two rapidly closing metal platens (i.e., "splat-cooled") before nucleation. It is shown that coarsening (i.e., "ripening") significantly alters solidification structures even at extremely rapid solidification rates.

4.0 Solute Redistribution

Sponsorship: Department of the Army

This program, now essentially complete, has been concerned primarily with solute redistribution in liquid and solid during dendritic growth. Computer programs have been formulated for determining extent of solid state diffusion to be expected during dendritic growth of binary alloys. Comparison of results with experiment has been excellent. Useful simplified mathematical expressions have also been formulated. Experimental and analytical work has also been conducted on more complex systems (e.g., ternary alloys).

5.0 Macrosegregation

Sponsorship: Department of the Army

This research comprises analytical and experimental study of macrosegregation (in ingot solidification). A general expression has been obtained for segregation caused by flow of solute-rich liquid to feed solidification and thermal contractions. It is shown that inverse segregation and centerline segregation can be understood as limiting cases of the analysis, and other types of segregation including macroscopic "banding" can result from the fluid flow. A factor of major importance in determining segregation that has not heretofore been considered is the direction of fluid flow with respect to solidification isotherms. Experiments agree qualitatively and quantitatively with analytical results.

6.0 Dendrite Morphology and Dendrite Arm Spacing

Sponsorship: Department of the Army

This program is part of a continuing study in our laboratory of dendrite structure, orientation, and grain size. Work during the last year has concentrated on factors influencing final dendrite arm spacing in cast alloys and it has been shown that coarsening ("ripening") exerts a major effect. Related work has been on details of dendrite structures in rapidly solidified aluminum alloys and directionally solidified tin alloys.

Technological interest in factors influencing dendrite structure, and particularly dendrite arm spacing, is high because of the strong influence of these factors on mechanical and other properties of cast materials (and wrought materials produced from cast ingots).

7.0 Inclusions

Sponsorship: Department of the Army, American Iron and Steel Institute

Several related activities are under way, designed to study the formation and growth of non-metallic inclusions in metal melts (especially in steel). Inclusion formation in the Fe-Si-O and Fe-S-O systems is being studied. Apparatus has been constructed to permit observation of dendritic growth and inclusion formation in metal melts during solidification. Alloys employed are low melting alloys; the solidification process is viewed microscopically using polarized light.

Inclusion formation is being studied in melts solidifying with essentially plane front. Finally, interaction of inclusions with solidifying dendrites is being studied by mechanical addition of "inclusions" to alloy melts.

8.0 Ultra-High Strength Aluminum Alloys

Sponsorship: Department of the Army

Influence of solidification heterogeneities on properties of wrought

aluminum alloys are being studied in this program. It has been shown that by careful control of solidification structure significant improvements in properties of wrought aluminum alloys can be obtained (e.g., tensile strengths in excess of 115,000 psi are obtained in rolled sheet).

In related work, study is under way of feasibility of obtaining "composite" structures in aluminum alloys similar to those previously obtained in lead-tin alloys (see Item 2 above). Study of properties of composites so produced is planned.

9.0 Hot Tearing

Sponsorship: American Foundrymen's Society

A new program has been initiated on influence of solidification variables on "hot tearing" (tendency of alloys to rupture during solidification).

Theses

F. R. Mollard, "Growth of Composites from the Melt", Sc.D. Thesis, Department of Metallurgy, January 1967.

R. W. Strachan, "A Technique for Levitation Melting, Undercooling and Splat Cooling of Metals and Alloys", Ph.D. Thesis, Department of Metallurgy, February 1967.

J. M. Coughlin, "Coarsening of Dendrites During Solidification", S. M. Thesis, Department of Metallurgy, January 1967.

J. Kaneko, "Effects of Convection on Structure of Metal Crystals", Sc.D. Thesis, Department of Metallurgy, August 1967.

Publications

M. C. Flemings, "Controlled Solidification", Strengthening Mechanisms, J. Burke, N. Reed, V. Weiss, Editors. Syracuse University Press, 1966 (Proceedings of the Twelfth Sagamore Army Materials Research Conference).

T. Z. Kattamis, M. C. Flemings, "Dendrite Structure and Grain Size of Undercooled Melts", Trans. Met. Soc., AIME, v. 236, 1966, pp. 1523-1532.

H. P. Utech, M. C. Flemings, "Thermal Convection in Metal Crystal Growth; Effect of a Magnetic Field", Crystal Growth, H. S. Peiser, Editor, Pergammon Press, 1967, pp. 651-658.

T. F. Bower and M. C. Flemings, "Formation of the Chill Zone in Ingot Solidification", Trans. Met. Soc. AIME, v. 239, 1967, pp. 216-219.

Papers Accepted for Publication

T. F. Bower and M. C. Flemings, "Structure of Dendrites at Chill Surfaces", accepted for publication, Trans. Met. Soc., AIME.

M. C. Flemings, G. E. Nereo, "Macrosegregation, Part I", accepted for publication, Trans, Met. Soc., AIME.

M. C. Flemings, R. Mehrabian, G. E. Nereo, "Macrosegregation, Part II", accepted for publication, Trans. Met. Soc., AIME.

M. C. Flemings, G. E. Nereo, "Macrosegregation, Part III", accepted for publication, Trans. Met. Soc., AIME.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt, Part I", accepted for publication, Trans. Met.. Soc., AIME.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt, Part II", accepted for publication, Trans. Met. Soc., AIME.

P. J. Ahearn, M. C. Flemings, "Dendrite Morphology of a Tin-Bismuth Alloy", accepted for publication, Trans. Met. Soc., AIME.

T. Z. Kattamis, J. M. Coughlin, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing of Aluminum-Copper Alloys", accepted for publication, Trans. Met. Soc., AIME.

T. F. Bower, M. C. Flemings, "Double Orientation of Cast Structures", accepted for publication, Trans. A.F.S., v. 75, 1967.

T. Z. Kattamis, M. C. Flemings, "Solidification of Highly Undercooled Castings", accepted for publication, Trans. A.F.S., v. 75, 1967.

T. Z. Kattamis, U. T. Holmberg, M. C. Flemings, "Influence of Coarsening on Dendrite Arm Spacing and Grain Size of Magnesium-Zinc Alloy", accepted for publication, J. Inst. Metals.

M. C. Flemings, "Directional Solidification", Proceedings Fourteenth Sagamore Army Materials Conference, Syracuse University Press (to be published).

M. C. Flemings, "Application of Theory to Solidification of Large Castings and Ingots", Proceedings Joint Conference on the Solidification of Metals, Brighton, England, December 4-7, 1967 (to be published).

Research Reports

M. C. Flemings, S. N. Singh, T. F. Bower, "Effects of Solidification Variables on the Structure of Aluminum Base Ingots", Annual Report Contract No. DA-19-020-ORD-5706(A), Frankford Arsenal, Contract Period June 1966-June 1967 (to be published).

T. Z. Kattamis, M. C. Flemings, "Solidification of Iron Base Alloys at Large Degrees of Undercooling", Interim Report, Contract No. DA-19-020-AMC-0231(X), Army Materials Research Agency, October 1965-October, 1966.

M. C. Flemings, R. V. Barone, H. D. Brody, "Investigation of Solidification of High Strength Steel Castings", Technical Report, Contract No. DA-19-020-ORD-5443(X), Army Materials Research Agency, Contract Period October 1965-October 1966.

F. R. Mollard, M. C. Flemings, "Growth of Composites from the Melt", Technical Report No. 2 to Office of Naval Research, November, 1966.

X-RAY AND ELECTRON OPTICS LABORATORY

Personnel

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

Professor R. E. Ogilvie, Professor
Professor T. O. Ziebold, Associate Professor of Nuclear Materials, Department of Nuclear Engineering
Dr. H. Harnsburger, Visiting Scientist
J. L. Bomback, Instructor and Graduate Student
S. Duerr, Research Assistant
W. J. Duffin, Research Assistant
R. H. Frost, Instructor and Graduate Student
N. G. Koopman, Research Assistant
P. K. K. Nayar, Research Assistant
A. Pinella, Research Assistant
A. Saffir, D. D. M.
L. Sutfin, D. D. M.
Karen Luciani, Secretary

Degrees Granted

J. L. Bomback, Sc.D., Metallurgy, June 1967
J. S. Duerr, S.M., Metallurgy, June 1967
W. J. Duffin, Sc.D., Metallurgy, June 1967
N. G. Koopman, Sc.D., Metallurgy, January 1967
P. K. K. Nayar, Sc.D., Metallurgy, June 1967
A. Pinella, S.M., Metallurgy, September 1967

Sponsorship

U. S. Atomic Energy Commission, AT(30-1)-3134, DSR 79855
Wright Air Development Center, AF33(657)-8906, DSR 76347
National Aeronautics and Space Administration, NsG-496(part), DSR 74568

Research Report

1.0 Phenomenology of Multicomponent Diffusion

Personnel: N. G. Koopman, P. K. K. Nayar

Sponsorship: U. S. Atomic Energy Commission

Diffusion experiments have been carried out at 1000°K in the Cu-Ag-Au ternary. In order to confirm the correlation of Onsager's extension of Fick's Law to multicomponent diffusion and the dependency of the diffusion flux to the atomic mobility and chemical potential, extensive activity measurements have been carried out in the Cu-Ag-Au ternary. The activity measurements were made in a zirconia solid state galvanic cell.

Diffusion experiments have been made in the Ag-Cu-Zn and Ag-Al-Zn systems. The third component, zinc, was diffused into the alloy single crystals from the vapor phase. The crystals were bent to different radii around an axis parallel to the (211) to introduce different concentrations of edge dislocations. The influence of the dislocations was investigated by measuring the penetration of the zinc.

2.0 Metallographic Studies of Craters and Ejecta Produced by Hypervelocity Impact

Personnel: A. Pinella

Sponsorship: National Aeronautics and Space Administration

For many years hypervelocity impact experiments were carried out with the purpose of studying crater formation and the laws which predict this process. Other recent aspects that have been included in the study of hypervelocity impact are: the possible chemical changes produced in the deformed material and metallurgical transformations that may occur in the target or ejecta.

This particular study has dealt with the study of metal transport from the projectile to the target material and metallographic features of the deformed material around the crater. Craters have been formed with projectiles traveling at 19.2 km/sec., 8.8 km/sec. and 2.7 km/sec. Sections taken through a crater have been studied with the electron microanalyzer and the scanning electron microscope.

3.0 Scanning Electron Microscopy of Fatigue Specimens

Personnel: R. H. Frost

Sponsorship: Wright Air Development Center

A scanning electron microscope was built to study the topology of iron whiskers. This instrument is now being used to study the nature of fractured surfaces and in particular, the deformation bands and cracks developed during fatigue. The unique feature of this instrument is the greater depth of field and greater magnification over conventional light microscopy. It also has the desirable feature that it is not necessary to replicate the surface to be studied as in normal electron microscopy.

4.0 Scanning Electron Diffraction

Personnel: J. L. Bomback

An electron diffraction unit was modified so that the diffraction patterns can be displayed on an x-y recorder or an oscilloscope. This instrument has been used to follow the crystallization kinetics of amorphous films and the order-disorder transformations in Cu_3Au films.

5.0 Study of Metallic Meteorites

Personnel: J. S. Duerr

Sponsorship: Smithsonian Astrophysical Observatory

A considerable amount of work has been done on the role of pressure, temperature, and time on the formation of the Wismanstatten pattern found in metallic meteorites. A cooling model with low internal pressure has been proposed for the development of the structures found in metallic meteorites. The plessite areas in metallic meteorites are now being studied with the scanning electron microscope. This instrument has enabled us to confirm the presence of martensite with a (259) habit plane.

6.0 Crystal Chemistry

Personnel: W. J. Duffin

Sponsorship: U. S. Atomic Energy Commission

This phase of research has been concerned with the factors which control the formation of C11, C40, and C54 type structures. The pseudo-binaries $ReSi_2$-$TiSi_2$, $TiSi_2$-$TiSb_2$ and $ReSi_2$-$ReAl_2$ have been investigated taking into account space filling, atom sizes, electron atom ratio, and electron configuration.

7.0 The Effects of Diet on the Microstructure and Microcomposition of Teeth

Personnel: A. Saffir, L. Sutfin

Sponsorship: National Institute of Dental Research

The topology and chemistry of rats teeth are being studied with the

aid of the scanning electron microscope and the electron microanalyzer. The aim of this work is to investigate the role of various minerals, that are introduced into the rats diet, on the structure of the teeth and how this might influence the dental caries rate. The distribution of flourine is of considerable interest in this work.

Publications

Z. Ban and R. E. Ogilvie, "The Role of Iron in the Oxidation of Molybdenum Disilicide," Trans. AIME, 236, (12), 1738-1742 (1966).

D. B. Brown and R. E. Ogilvie, "An Electron Transport Model for the Prediction of X-ray Production and Electron Backscattering in Electron Microanalysis," J. Appl. Phys., 37, (12), 4429-4433 (November 1966).

R. E. Ogilvie, "Electron Microanalysis of Paint Samples from the Bersheh Sarcophagus," Applications of Science in Examination of Works of Art, Proceedings of the Seminar, September 1966, Museum of Fine Arts, Boston.

R. E. Ogilvie and T. O. Ziebold, "Ternary Diffusion in Cu-Ag-Au Alloys," Trans. AIME, 239, p. 942 (1967).

A. Saffir and R. E. Ogilvie, "The Effects of Diet on the Microstructure of Teeth," Proceedings of Second National Conference on Electron Microprobe Analysis, June 1967.

T. O. Ziebold, "Precision and Sensitivity in Electron Microprobe Analysis, Analytical Chemistry, 39, p. 858, July 1967.

STRUCTURAL MATERIALS

THE RELATIONSHIP BETWEEN MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CEMENTITIOUS MATERIALS

Personnel

Professor F. J. McGarry, Professor, Civil Engineering
Professor R. B. Williamson, Assistant Professor, Civil Engineering
C. B. Doughty, Research Assistant, Civil Engineering

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78898

Research Report

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.

DEFORMATION OF ALPHA IRON SINGLE CRYSTALS

Personnel

Professor R. C. Jones, Associate Professor, Civil Engineering
W. A. Maude, Graduate Student, Civil Engineering
D. Newman, Part-time Student Assistant

Degrees Granted

D. R. Heerwagen, S.M., Civil Engineering, January 1967.
W. A. Maude, Materials Engineer, Civil Engineering, June 1967

Sponsorship

Advanced Research Projects Agency, SD-90, DSR 78898

Research Report

The Schulz x-ray diffraction topography technique was employed to study the structure of high-purity alpha-iron single crystal plates produced by the strain-anneal method. The crystal structure was investigated at various stages in the growth process, after growth was complete, after each addition in a series of incremental strains, and after the crystals had been shaped by various processes.

The study revealed that improvements in microfocus x-ray generators, with resultant increase in the resolution obtainable, and the advent of the Polaroid x-ray camera which greatly reduces the set up time required, have made the Schulz technique a practical and useful tool for metallurgical research. The technique permits reaching structure levels that cannot be reached by light optical methods.

The topographs obtained permitted insight into the nature of the crystal growing process. The Schulz technique was found to be far more sensitive than light optical metallography in detecting changes in structure resulting from the addition of small incremental strains

at low strain levels. However, it was found that the Schulz technique becomes useless when the strain level reaches 5 to 10%, the limit varying with the orientation of the crystal.

When used to study the effects of various shaping processes on the structure of the crystals, the Schulz technique revealed that spark erosion machining did not produce strain free specimens as had been presumed. As a result, the spark erosion machining process was modified to improve the results. When tried on surfaces that had been produced by mechanical means, the technique was found to be of little value. The strain introduced into the surface layer was too great.

The over-all conclusion that can be drawn from this study is that the Schulz technique is an extremely useful tool for investigating metals that are relatively strain free, and for following the deformation of metals at low strain levels.

Publications

W. A. Maude, R. C. Jones, and R. B. Williamson, "X-ray Diffraction Topography of As-grown and Deformed Alpha-Iron Single Crystals", MIT Civil Engineering Department Report #R67-18, p. 149, May 1967.