MATERIALS RESEARCH CENTER
NORTHWESTERN UNIVERSITY
1967 ANNUAL REPORT

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DEPARTMENT OF DEFENSE

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REPORT PERIOD

1 OCTOBER 1966 to 30 SEPTEMBER 1967

Also included in this report is the description of materials research for which support has also been received from the following agencies:

1. Aerospace Research Laboratory, Wright-Patterson Air Force Base.
2. Air Force Office of Scientific Research.
3. American Iron and Steel Institute.
4. Atomic Energy Commission.
5. Joint Services Contract, Army, Navy and Air Force.
6. National Institutes of Health.
7. National Science Foundation.
8. Northwestern University Research Committee.
9. Office of Naval Research.
10. Petroleum Research Fund.
11. U. S. Army Research Office, Durham.
12. Walter P. Murphy Fund, Northwestern University.

The source of the main support of each project is indicated after the title of each research report.

MATERIALS RESEARCH CENTER
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

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Research Reports

INTRODUCTION

The Northwestern University Materials Research Center was established 1 July 1960, after the Advanced Research Projects Agency of the Department of Defense awarded a major contract to the University for the purpose of conducting an expanded and coordinated interdisciplinary interdepartmental program of basic research and graduate education in materials. By materials is meant here mainly the solid state although pertinent and related research in other fields is sometimes included. The Materials Research Center provides financial support for research conducted by the faculty of the College of Arts and Sciences and the Technological Institute and their graduate students and postdoctorals, and has a major hand in the operation of central research facilities.

The Materials Research Center is administered by a committee reporting to H. B. Gotaas, Dean of the Technological Institute. In addition, there is a Materials Research Center Advisory Committee composed in part of the Chairmen of the Departments involved. During the 1966-67 year these chairmen were as follows: D. S. Berry, Civil Engineering; D. D. DeFord, Chemistry; H. M. Hulburt, Chemical Engineering; J. A. Marcus, (Acting Chairman) Physics; G. J. Murphy, Electrical Engineering; and J. Weertman, Materials Science.

The Chairmanship, Associate or Assistant Chairmanship and Committee Memberships of the Materials Research Center Committee are rotating positions. The composition of the Committee during the period of this report is given below. Professor D. H. Whitmore became the Associate Chairman of the Committee 1 September 1967, replacing Professor J. B. Wagner, Jr., who was the Assistant Chairman. Membership of R. L. Hines, Physics, terminated 31 August 1967 and J. A. Marcus, Physics, was appointed in his place for the usual three-year period.

This eighth report is for the most part a compendium of the reports of the individual researches supported largely or substantially with funds derived from the ARPA Contract. Other agencies also sponsor some of the research; these agencies are listed on the title page and are also indicated in the individual reports. Inasmuch as the Washington Office of ARPA requires the reporting on the progress and achievements of each individual's research, by means of the Government's 1498 Forms, where the research is mainly supported by ARPA, we have reported on all of our researches using this general 1498 Form format. Where an individual professor has more than one project, i.e., more than one 1498 Form, a list of his publications and invited talks is given at the end of the separate projects. The names of the co-workers on each project are also given as in previous reports.

There is, of course, research in the materials field in which ARPA support plays a role only through the use of facilities. Such research is also described in this report, and all Ph.D. thesis dissertations in the field completed during the year are listed. The main financial support of each of these researches and students is indicated.

Some brief comments on the research program precede this compendium.

In this report we have included a listing only of those publications which have already appeared; not those accepted or submitted for publication.

The Materials Research Center Committee gratefully acknowledges the assistance of its secretarial staff, Mrs. Jo-Ann F. Anderson and Mrs. Irene E. Butler.

Materials Research Center Committee, 1966-67

A. L. Allred, Chemistry
J. O. Brittain, Materials Science
W. W. Graessley, Chemical Engineering
R. L. Hines, Physics
T. Mura, Civil Engineering
J. B. Wagner, Jr., Assistant Chairman
M. Dole, Chairman

COMMENTS ON THE RESEARCH PROGRAM

Thirty-six basic research programs in materials by thirty-seven faculty members in six different departments of the College of Arts and Sciences and of the Technological Institute constitute the present Materials Research Center Program. This is the same number of research programs as during the previous year because, although a new project was initiated, that of Professor James T. Waber of the Department of Materials Science, an old project was terminated, that of Professor R. J. Cashman of the Department of Physics.

Not counting the ARPA support of the central facilities, the available ARPA funds were distributed to research projects in the several departments approximately as follows: Materials Science, 37%; Physics, 23%; Chemistry, 19%; Electrical Engineering, 10%; Civil Engineering, 8% and Chemical Engineering, 3%.

Professor Martin Bailyn, Physics, spent the year as a visiting professor at the University of Leeds, England and Professor J. B. Cohen, Materials Science, at the London Branch of the Office of Naval Research as its Scientific Liaison Officer for Materials Science. James T. Waber, Materials Science, joined the faculty as a full professor 1 January 1967. The contributions of Professors Bailyn and C. T. Walker, both of whom were in England at the time of compiling this report, were not received in time to be included in this volume.

As in the past, we now describe some of the research highlights of the year covered by this report. This year the discussion will chiefly be devoted to the research of members of the Center whose work has not been highlighted in recent former reports. For a more complete picture of the research accomplishments of the Center the comments on the research contained in the Annual Technical Reports for 1965 and 1966 should be consulted. The present comments are described in alphabetical order of the author's names.

The joint team of Professors Achenbach and Herrmann of the Civil Engineering Department have used the fundamental balance laws of mechanics and the theory of thermodynamics of simple materials to study the propagation of a mechanical disturbance through a viscoelastic medium with temperature dependent properties. The non-linear differential equation governing the growth or decay of a stress wave as it propagates through the medium was solved for the case of small strains. The influence of heat conduction was investigated, leading to the conclusion that in a conductor and a non-conducto the jumps in entropy at the wave fronts are of the order of the strain and the strain cubed, respectively.

Professor Brittain of the Materials Science Department and his group have shown that the overshoot phenomena in Cu-15 at.% Al single crystals are intimately related to the formation of short lengths of the Lomer-Cottrell locks which act as forest type obstacles to conjugate slip. It was further demonstrated that the overshoot was independent of the stacking fault energy in the range of 5 to 10 ergs cm^{-2} for a Cu-15 at.% Al alloy. They further

found that the optical properties of NiAl, CoAl, NiGa and CoGa indicate a free electron like behavior below phonon energies of about 1 e.v. The prominent compositional dependent absorption band at 2.5 e.v. in NiAl is absent in CoAl, CoGa and NiGa.

Professors Brust and Liu of the Physics Department have cooperated in completing a theoretical study of the changes in the atomic form factor in semiconductor crystals subjected to enormously high hydrostatic pressures. From the results of this work they can derive the change of the entire band structure with stress and the pressure dependence of the optical properties. They can also predict the change with pressure of a number of other properties such as effective mass, transport properties, carrier symmetry and the like. In addition, they have investigated theoretically the formation of impurity resonances around charged impurities in α-Sn whose energy gap is identically zero. It would be interesting to see an experimental verification of the impurity resonances that they have predicted for this case.

In work also concerned with a zero gap semiconductor Professor Ewald of the Physics Department and his co-workers have succeeded for the first time in separating the degenerate conduction and valence bands. This results in typical (but controllable) intrinsic semiconductor behavior in a temperature region in which the properties of other semiconductors are dominated by impurities. They also found a $T^{3/2}$ mobility temperature dependence for acoustical phonon scattering which had not previously been observed for holes. Its appearance in gray tin is presumably due to the existence of only one valence band that can be thermally populated with holes.

Professor Freise and his students of the Materials Science Department have succeeded in demonstrating that the allotropic transformation of the cobalt matrix plays a dominant role in determining the mechanical properties of the binary and ternary alloys investigated. In addition, the allotropic transformation has been used to refine the grain size in cobalt-base alloys. It is envisioned that a thorough understanding of this allotropic transformation in cobalt base alloys and its effect on mechanical properties will permit the development of alloys with a wider range of useful properties for both high temperature and corrosion resistant applications.

Professor Graessley of the Chemical Engineering Department has developed a theoretical method of predicting quantitatively the viscosity-shear rate behavior of a polymer system from its molecular weight distribution. The recent measurements carried out by his group on branched, polydisperse polyvinyl acetate have shown that the intrinsic viscosity can yield significant information on structure even in complex systems. Since branching strongly affects many properties, the determination of branching by this characterization scheme should be of help in achieving better control of the polymer during the polymerization process.

Professor Hofacker of Chemistry and his group of theoreticians have made significant progress in developing formal expressions for protonic semiconductor properties in hydrogen bonded solids. Work has been completed on the prediction of collective excitations in a one-dimensional hydrogen bonded ferroelectric. Their spectra were calculated for the first time over

the whole temperature range, including all significant interactions between hydrogen bonds. Professor Hofacker is now conferring with experimentalists in a number of schools to see if his theories can serve as a guide in the interpretation of the experimental data.

In our 1964 Annual Report the new theory of sintering of Professor Johnson of the Materials Science Department was discussed. Johnson and his students have now found that by measuring one additional parameter, the neck size between particles, they can determine surface diffusion coefficients. Published data of these three diffusion coefficients obtained during the sintering of compacts of uniform spherical particles of iron agree closely with the theoretically calculated values. This work should help in the understanding of the basic mechanism of sintering used in the production of piezo and ferroelectric materials, ceramic magnets, high frequency and high temperature insulators, etc.

Professor Kannewurf and his students of the Electrical Engineering Department have demonstrated that the superconductivity of the Tl-Te is a true effect of the γ-phase with a maximum T_c at the concentration 61% thallium. The experimental observations are compatible with existing theories that predict the occurrence of superconductivity in either n-type or p-type semiconductors and semimetals. Only three or four materials at present are known to be examples of this type of superconductor.

Professor Kauffman of the Materials Science Department and his group have added significantly to the understanding of recovery phenomena of fcc metals electron irradiated at low temperatures. A theoretical model has been developed which involves mainly the nature of intensified migration occurring at low temperatures. They have determined quantitatively for the first time the order of the reaction which has been interpreted in terms of a model involving low concentration interstitial impurity interactions and, at higher concentrations, a series of more complex interactions between interstitials. The amount of recovery due to free interstitial recombinations with vacancies decreases in the order copper to silver to gold.

Finally, it should be mentioned that Professor Waber of the Materials Science Department, who joined the faculty 1 January 1967, is the Editor of a book on Energy Bands in Metals and Alloys. This book represents an up-to-date statement of progress towards obtaining reliable energy band curves for all the metals.

DOCTOR OF PHILOSOPHY DEGREES AWARDED IN THE FIELD OF MATERIALS

JUNE COMMENCEMENT 1967

Louis M. Alberino. Chemical Engineering. "Radiation Induced Changes in the Molecular Weight of Polystyrene in the Pre-Gel Region". ARPA

Lloyd Berrin. Materials Science. "Volume and Grain Boundary Diffusion During Sintering and the Sintering Kinetics of Nickel". ARPA

Bruce L. Booth. Physics. "Magnetoresistance Oscillations in Antimony Doped Gray Tin". ARPA

Lee W. Bush. Chemistry. "Electron Spin Resonance Studies of Some Unsubstituted and Substituted Aromatic Radical Anions". TA, NIH, ARPA

Harry E. Cook. Materials Science. "Interdiffusion in Silver-Gold Solid Solutions at Low Temperature". ARPA, WPM, Cabell, NSF

Didier de Fontaine. Materials Science. "A Computer Simulation of the Evolution of Coherent Composition Variations in Solid Solution". ARMY

John B. Dinklage. Electrical Engineering. "Soft X-ray Diffraction by Multi-layered Thin Film Structures and Their Interdiffusion". ARPA, NSF

Carl W. Fairhurst. Materials Science. "The Crystallography of Dental Amalgam". ARPA, No Stipend

Anthony F. Giamei. Materials Science. "Solid State Phase Equilibria in Cobalt Rich Co-WC Alloys". WPM, NSF, Cabell, ARPA

Malcolm P. Johnson. Chemistry. "Lewis Basicity of Metals". TA, NSF, NIH

Orville F. Kimball. Materials Science. "Investigation of the Pre-precipitation Process in the Au-Ni System". ARPA

Frederick B. Koch. Materials Science. "Ordering in Non-Stoichiometric Fe_xO". Cabell, AF

Paul M. Kuznesof. Chemistry. "Mass Spectrometric and Theoretical Studies of Boron-Nitrogen Systems". TA, ARPA, NIH

Philip N. LaMori. Materials Science. "Compressibility of Rocks and Minerals to 450°C and 36 kb and Their Application to the Upper Mantle". ARPA

Eugene P. Lautenschlager. Materials Science. "The Effects of Structure Upon the Mechanical Behavior of β-NiAl". ARPA

Harris L. Marcus. Materials Science. "Precipitation in the Fe-Mo System". NASA, ARPA

Ramiro A. Montalvo. Physics. "Magnetic Anisotropy in Antiferromagnetic Chromium". ARPA

David R. J. Owen. Civil Engineering. "Continuum Theory of Dislocations". ARPA

Paul S. Poskozim. Chemistry. "Chemistry of Trichlorogermanate(II) Salts". Ta, ARPA

Karl B. Rundman. Materials Science. "Decomposition in Aluminum-Zinc Alloys". ARPA, WPM, ARMY

John J. Rupp. Chemistry. "Cyanide Bridge Compounds with the Group Four Metal Tetrafluorides". ARPA, NIH

John W. Schwartz. Physics. "Phonon Resonances in Some Alkali Halides Doped with Divalent Ions". ARPA

Martin A. Seitz. Materials Science. "Electronic Drift Mobilities and Space-Charge-Limited Currents in Lithium Doped Zinc Oxide". ONR

George P. Sendeckyj. Civil Engineering. "Ellipsoidal Inhomogeneity Problem". ARPA

Paul H. Shingu. Materials Science. "Effect of Competitive Mechanics Upon Densification During the Initial Stage of Sintering and Sintering Kinetics of Iron". ARPA

Gerald P. Wirtz. Materials Science. "Precipitation from Magnesiowustite Solid Solution". AF

Frederick W. Wiffen. Materials Science. "Production and Stage I Recovery of Electrical Resistivity in Electron Irradiated Noble Metals". ARPA, Barker

Ronald M. Wolosewick. Mechanical Engineering. "Studies in Viscoelastic Wave Propagation". ARPA

Kenneth R. Zanio. Materials Science. "A Study of the Defect Structure of Lead Sulfide". ONR, NSF

Research supported by agencies as indicated:
AF, Air Force Office of Scientific Research or Wright Patterson Air Force Base
ARMY, Army Office of Research
ARPA, Advanced Research Projects Agency
Barker (Northwestern University Fellowship)
Cabell (Northwestern University Fellowship)
NASA, National Aeronautics and Space Administration
NIH, National Institutes of Health
NSF, National Science Foundation
ONR, Office of Naval Research
TA, Northwestern University Teaching Assistantship
WPM (Northwestern University Walter P. Murphy Fellowship)

DISSIPATION OF ENERGY DUE TO COUPLING OF THERMAL AND MECHANICAL EFFECTS

J. D. Achenbach
Associate Professor, Department of Civil Engineering

G. Herrmann
Professor, Department of Civil Engineering

D. P. Reddy
Ph.D. Thesis Research

S. M. Vogel
Ph.D. Thesis Research

Objective

The study of damping phenomena in materials due to viscosity and due to the coupling of mechanical and thermal disturbances. Particular attention is devoted to the influence on propagating stress discontinuities of thermomechanical coupling, temperature dependent material properties, non-linear material behavior and large deformations. This study will supply information on the behavior of materials subjected to impact loads.

Approach

The fundamental balance laws of mechanics and the theory of thermodynamics of simple materials are used. In this work the free energy not only depends on the present values of the strains and the temperature, but also on the histories of these quantities. Relations are established between the various discontinuous quantities at the wave fronts: stress, strain, entropy and temperature gradient. The differential equation governing the growth or decay of a stress wave as it propagates through the medium is solved. The method is extended to obtain Taylor expansions for the stresses after the wave front has passed. The conditions governing the formation of shocks are established.

Progress

A study was completed on the influence of thermal conductivity and temperature dependent material properties on stress wave propagation in viscoelastic solids. Whereas for a heat conducting solid the jump in entropy at the wave front is of the same order as the strain, for a non-conductor this jump is of order strain-cube. The propagation of isothermal disturbances in finite strain was studied for longitudinal and shear loading. The coalescence of simple waves into a shock was investigated.

PUBLICATIONS

"Note on Wave Propagation in Linearly Viscoelastic Media," J. D. Achenbach and D. P. Reddy, Zeitschrift für angewandte Mathematik und Physik, 18, 1, 141 (1967).

"Shear Waves in Finite Strain Generated at the Surface of a Viscoelastic Half-Space," J. D. Achenbach and D. P. Reddy, Int. J. of Eng. Sci. 5, 527 (1967).

"The Propagation of Stress Discontinuities According to the Coupled Equations of Thermoelasticity," J. D. Achenbach, Acta Mechanica III, 342 (1967).

"Shear Waves in Finite Elastic Strain," J. D. Achenbach, Quarterly of Applied Mathematics, 25, 3, 306 (1967).

"On Stress Waves in Viscoelastic Media Conducting Heat," J. D. Achenbach, S. M. Vogel and G. Herrmann, Proceedings of IUTAM Symposium on Irreversible Aspects of Continuum Mechanics, Springer-Verlag (1967).

DYNAMIC THEORIES OF FIBER REINFORCED COMPOSITES

J. D. Achenbach
Associate Professor, Department of Civil Engineering

G. Herrmann
Professor, Department of Civil Engineering

C-T Sun
Ph.D. Thesis Research

This research is supported by the Office of Naval Research.

Objective

To establish a continuum theory governing the dynamic behavior of fiber reinforced composites and laminates.

Approach

Approximate displacement expressions for the discrete elements are used to compute potential and kinetic energies for a volume element of the composite. By means of a smoothing operation, energy densities for the composite are derived. Application of Hamilton's principle, where certain subsidiary conditions enter through the use of Lagrangian multipliers, yields displacement equations of motion, constitutive equations and boundary conditions.

Progress

An effective stiffness theory for fiber reinforced and laminated composites was proposed which can account for such dynamic effects as dispersion of time harmonic waves. Various versions of the general theory were investigated and their relative merits were established. The relation of these theories to the theories of elasticity with couple stresses and with microstructure were explored.

INVITED TALKS

"Applications of Theories of Generalized Cosserat Continua to the Dynamics of Composite Materials," IUTAM Symposium on the Generalized Cosserat Continuum Theory, Freudenstadt and Stuttgart, Germany, August (1967).

"Enlarging the Relevance of Theories of Solids with Micro-Structure," IBM Research Laboratory, Rüschlikon, Switzerland, March (1967).

"Dynamics of Heterogeneous Solids," Sandia Corporation, Albuquerque, New Mexico, February (1967).

"Effective Stiffness Theory for a Laminated Composite," Tenth Midwestern Mechanics Conference, Fort Collins, Colorado, August (1967).

"Propagation of Time-Harmonic Waves in Fiber-Reinforced Composites and Laminates," Michigan State University, East Lansing, Michigan, October (1967).

"Wave Propagation in Laminated and Fiber-Reinforced Composites," International Conference on the Mechanics of Composite Materials, Philadelphia, Pennsylvania, May (1967).

ESR OF ANION RADICALS OF POLYPHENYLS AND THEIR DERIVATIVES

A. L. Allred
Associate Professor, Department of Chemistry

L. Bush
Ph.D. Thesis Research (completed)

P. Hoyer
Ph.D. Thesis Research

L. Newman
Ph.D. Thesis Research

Objective

To study the "distribution" of the unpaired electron in moderately long-chain molecules, to prepare stable organometallic free radicals, and to study the characteristics of bonds between substituents and aromatic rings.

Approach

Anion radicals were generated by either electrochemical or alkali metal reduction, and the electron spin resonance spectra were obtained for dilute solutions at various temperatures. The parent compounds were investigated by ultraviolet spectroscopy and by A.C. and D.C. polarography.

Progress

The following radicals were studied: 1,4-bis(trimethylsilyl)benzene, 1,4-bis(trimethylgermyl)benzene, terphenyl (all polyphenyls here are bonded in <u>para</u> positions), 4,4″-bis(trimethylsilyl)terphenylide, 4,4″-bis(trimethylgermyl)biphenylide, quarterphenylide, 4,4‴-bis(trimethylsilyl)quaterphenylide, 4,4‴-bis(trimethylgermyl)quaterphenylide, quinquephenylide, sexiphenylide, 4,4⁗-bis(trimethylsilyl)sexiphenylide, 4,4′-difluorobiphenylide, 3,3′-difluorobiphenylide, and 2,2′-difluorobiphenylide. The anion radicals, of all the terphenyl and quaterphenyl derivatives, are stable indefinitely at room temperature in the absence of air. The observed coupling constants, ultraviolet spectra, and polarograms agree well with the results predicted by simple molecular orbital calculations. Previously published heteroatom parameters and π-bond orders for the silicon-carbon and germanium-carbon bonds were confirmed. The formation of both monoanions and dianions by all of the terphenyl and quaterphenyl compounds was observed by A.C. and D.C. polarography and the corresponding reduction potentials were measured.

INVITED TALKS

Organizer of a symposium on "Organometallic Radicals," National Meeting of the American Chemical Society, Miami, Florida, 12 April 1967.

ATTEMPT TO PREPARE HgF_3

A. L. Allred
Associate Professor, Department of Chemistry

C. F. Shaw
Ph.D. Thesis Research

Objective

To prepare a compound having an element with an oxidation state higher than the group number. This project was prompted by the recent preparation of many compounds of the noble gases (Group 0) and by the low magnitude of the third ionization potential of mercury.

Approach

The preparative reactions are being carried out at the Argonne National Laboratory in a vacuum line constructed from Monel, copper, and Kel-F. Fluorine has been added to systems containing either mercuric fluoride or mercuric fluoride plus cesium fluoride, with and without the solvent fluoride. Cesium fluoride was added in an attempt to obtain a complex, $CsHgF_4$ or Cs_3HgF_6.

Progress

Some evidence, still inconclusive, has been obtained for excess oxidizing ability of mercury after the removal of unreacted fluorine, suggesting Hg(III).

ISOTOPE EFFECTS IN 2,4-PENTANEDIONE

A. L. Allred
Associate Professor, Department of Chemistry

D. W. Thompson
Ph.D. Thesis Research (completed)

Objective

To measure the relative tendencies of protium and deuterium to form intramolecular hydrogen bonds.

Approach

Isotope effects in 2,4-Pentanedione and 2,4-Pentanedione-$3d_2$ were investigated by proton magnetic resonance, infrared spectroscopy, and ultraviolet spectroscopy.

Progress

The change in the keto-enol tautomeric equilibrium resulting from deuterium substitution at the methylene carbon was measured at various temperatures. The enthalpy change for enolization of the protium-containing compound is more negative than for the deuterium-containing compound. In contrast, deuterium forms stronger hydrogen bonds than protium in most systems involving intermolecular hydrogen bonds. For the reactions giving the enol tautomers in the above protium and deuterium systems, $\Delta H = -2.43 \pm 0.17$ kcal/mole and -0.096 ± 0.045 kcal/mole and $\Delta S = -5.23 \pm 0.60$ e.u. and $+2.57 \pm 0.16$ e.u., respectively. Thus, the isotope effect in this system is astonishingly large.

Partial substitution of deuterium at the terminal methyl groups and at the 3-position in the keto tautomer shifted the proton resonance peaks up-field.

LEWIS ACID-BASE ADDUCTS OF β-DIKETONES

A. L. Allred
Associate Professor, Department of Chemistry

D. W. Thompson
Ph.D. Thesis Research (completed)

Objective

To prepare and characterize new compounds having metal ions bonded to the carbonyl groups of ligands containing the $-C(O)-CY_2-C(O)-$ unit.

Approach

Metal halides were combined with acetylacetone or other β-diketones in various inert solvents under a nitrogen atmosphere.

Progress

Analytical, nuclear magnetic resonance and infrared data are consistent with the following new complexes being simple 1:1, non-ionic adducts: $SnCl_4(C_7H_{12}O_2)$ (prepared from 3-methylacetylacetone), $TiCl_4(C_7H_{12}O_2)$, $TiBr_4(C_7H_{12}O_2)$, $TiI_4(C_7H_{12}O_2)$, $ZrCl_4(C_7H_{12}O_2)$, $SnCl_4(C_6H_{10}O_2)$ (prepared from 3-methylacetylacetone), $SnCl_4(C_5H_8O_2)$ (prepared from acetylacetone), and $TiCl_4(C_5H_8O_2)$.

During the past 65 years several conflicting publications have indicated that the reaction of tin tetrachloride and acetylacetone gives at least one other product in addition to cis-dichlorobis(acetylacetonato)tin(IV). In the current research, the adduct, $SnCl_4(C_5H_8O_2)$ was isolated from this reaction at)°C.

NUCLEAR MAGNETIC RESONANCE OF t-BUTYL GROUPS

A. L. Allred
Associate Professor, Department of Chemistry

W. Wilk
Ph.D. Thesis Research

Objective

To study factors which determine the magnitudes of chemical shifts in nuclear magnetic resonance.

Approach

Proton chemical shifts of butyl groups were accurately measured at low concentrations in the magnetically isotropic solvent carbon tetrachloride.

Progress

Data for 35 organic and organometallic compounds have been collected and the results are being compared with the prediction of current theories.

BIS(TRIPHENYLPHOSPHINE)GOLD(I) HALIDES

A. L. Allred
Associate Professor, Department of Chemistry

J. M. Meyer
Ph.D. Thesis Research (completed)

This research is supported by the National Institutes of Health.

Objective

To prepare and characterize complexes of gold(I) having a coordination number of two and to form metal-metal bonds from these complexes by reduction.

Approach

Bis(triphenylphosphine)gold(I) chloride, bis(triphenylphosphine)gold(I) bromide, and bis(triphenylphosphine)gold(I) iodide were prepared by the addition of excess triphenylphosphine to the simple (triphenylphosphine)-gold(I) halide in acetone.

Progress

Infrared, molecular weight and conductivity data were obtained for the bis(triphenylphosphine)gold(I) halides. Crystals of the compounds are stable in air and contain the bis(triphenylphosphine)gold(I) cation. In solution, the compounds dissociate reversibly to give triphenyl-phosphine and mono(triphenylphosphine)gold(I) halide.

PUBLICATIONS

"Ultraviolet Spectra of Biphenyl Derivatives of Group IV-B," M. D. Curtis, R. K. Lee and A. L. Allred, J. Am. Chem. Soc., 89, 4000 (1967).

ORGANOGERMANIUM COMPOUNDS

A. L. Allred
Associate Professor, Department of Chemistry

C. F. Shaw
Ph.D. Thesis Research

This research is supported by the National Institutes of Health.

Objective

The major goal here is the synthesis of tetra-t-butylgermane which should be an outstanding example, if not the best example, of a nearly spherical molecule. Fisher-Taylor-Hirschfelder models are consistent with this prediction. The physical properties, including the heat capacity, the crystal system(s), phase transitions, and cryoscopic constant, will be measured and should be interesting in view of the compact structure.

Approach

From a consideration of silicon chemistry, the optimum conditions for the preparation of tetra-t-butylgermane involve the reaction of t-butyllithium with tri-t-butylgermanium fluoride in n-octadecane at approximately 225°C. Tri-t-butylgermanium fluoride should be obtainable from the corresponding chloride by treatment with ethanol-hydrofluoric acid.

Progress

Di-t-butylgermanium dichloride and tri-t-butylgermanium hydroxide have been prepared.

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS-STACKING FAULTS IN A Cu-15 AT.% Al ALLOY AND THEIR RELATIONSHIP TO LATENT HARDENING

J. O. Brittain
Professor, Department of Materials Science

M. Meshii
Professor, Department of Materials Science

T. Tisone
Ph.D. Thesis Research

Objective

To investigate the role of stacking fault energy, SFE, on the tensile properties of Cu-15 at.% Al alloy single crystals. The latent hardening phenomena of overshooting was the primary concern.

Approach

Electron transmission microscopy and mechanical tests were used to evaluate structure and properties of the single crystals. SFE was determined using measurements from threefold nodes, intrinsic-extrinsic fault pairs and Frank triangles.

Progress

The SFE, which exhibited a reversible temperature dependence, increased with increasing temperature for both intrinsic and extrinsic faulting. The ratio of extrinsic to intrinsic fault energy was found to be 1.14 ± 0.08. Some complex fault configurations such as Lomer-Cottrell locks, etc., and a new type of fault designated as a H-fault were considered. The conjugate slip system was the most important secondary slip system and forest dislocation interactions between primary and conjugate dislocations forming short lengths of Lomer-Cottrell dislocations were responsible for the latent hardening of the conjugate system. The densities of conjugate dislocations and subsequent Lomer-Cottrell interactions increased with increasing strain during stage II work hardening. Overshoot was found to be independent of orientation and test temperature but appeared to increase with increasing quench temperature. It was concluded that overshoot was not a direct function of SFE in the range of 5 to 10 ergs/cm^2 for a Cu-15 at.% Al alloy. A model for the termination of overshoot is based upon the collapse of segments of Lomer-Cottrell dislocations under the line tension of bowed out conjugate dislocation segments.

PUBLICATIONS

"Lomer-Cottrell Locks in Cu-15 at.% Al Alloys," T. Tisone, M. Meshii and J. O. Brittain, Phil. Mag. 16, 647 (1967).

"Electron Transmission Microscopy of NiAl," E. P. Lautenschlager, T. C. Tisone and J. O. Brittain, Physica Status Solidi 20, 443 (1967).

"Slip in Hard Sphere CsCl Models," E. P. Lautenschlager, T. Hughes and J. O. Brittain, Acta Met. 15, 1347 (1967).

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS-GALVANOMAGNETIC EFFECTS IN β′-NiAl

J. O. Brittain
Professor, Department of Materials Science

Y. Yamaguchi
Postdoctoral Research Associate

Objective

Study the electronic properties of an alloy that has a variation of defect structure and electron concentration with composition.

Approach

The alloy investigated was β′-NiAl which has a B2 crystal structure (isotypic with CsCl) and displays a defect structure, i.e., Ni vacancies are present in alloys containing more than ~51 a/o Al while substitutional Ni defects are present in alloys with Ni > 50 a/o Ni, and substitutional Al defects occur in the compositional range of 50-51 a/o Al.

Alloys of β′-NiAl with controlled concentration of defects (controlled deviation from stoichiometry) were prepared. The effects of defect structure and electron concentration upon electrical resistivity, Hall coefficient, and transverse magnetoresistance were ascertained by appropriate measurements at 4.2°, 77° and 298°K.

Progress

The electrical resistivity measurements indicate that β′-NiAl are metallic but poor conductors. The variation of resistivity with composition indicates that the point defects tend to cluster as the composition departs from stoichiometry. The Hall coefficient was positive while the magnetoresistance was small but negative in sign except for compositions near the phase boundaries where the sign of both measurements is reversed. These results imply that a two band model may be necessary to explain transport processes in NiAl.

THE DISLOCATION ANALYSIS OF STRESS WITH APPLICATIONS TO PLASTICITY AND WORK HARDENING

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J. D. Buch
Ph.D. Thesis Research

This research is supported by the Office of Naval Research and the Walter P. Murphy Foundation of Northwestern University.

Objective

To develop and utilize a consistent analysis for determining the tensor dislocation density configuration giving rise to an assumed, derived, or known stress field. The motivation behind the approach is that it is easy to postulate stress fields which will result in reasonable values for mechanical properties, and it is desirable to find dislocation configurations which will satisfy the stress model.

Approach

The approach is based upon the continuum theory of dislocations. It can be shown that the dislocation density can be divided into two parts, one of which is known to give rise to stress fields. Therefore all the dislocations causing the stress are contained in the other term which can be expressed directly in terms of the stress field and elastic constants. The approach consists of simply calculating this term.

Progress

All the necessary theorems have been proven. Specific examples have been presented in which the dislocations derived by the dislocation analysis of stress can be shown by stress analysis of dislocations to give the correct results. The dislocation theory of beam bending in plane stress and plane strain has been analyzed. A novel feature is the appearance of anti-elastic plastic bending in plane stress and good agreement with experiment is found. Some results are also available for punch indentation. The circular cylindrical edge pile-up under arbitrary plane loading is calculated. The elliptical cylindrical edge pile-up under homogeneous shear or tensile loading has been discussed, as well as the elliptical cylindrical screw dislocation pile-up under arbitrary loading. The application of these calculations to dislocation braids and tangles and a discussion of work-hardening theories is in the process of completion.

STRUCTURE SENSITIVE PROPERTIES OF INTERMEDIATE SOLID SOLUTIONS

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

Objective

This investigation is directed towards discerning the role of defects in an intermediate solid solution upon various physical and optical properties.

Approach

The optical constants were computed from data taken on a specially designed reflectometer that was used in conjuction with a Zeiss MM12 double prism monochromater. Electrical resistivity was measured at 4.2 and 297°K by the usual potentiometric method.

Progress

The optical properties of NiAl, CoAl, NiGa and CoGa indicate that some of the alloys show free electron like behavior below photon energies of about 1 eV. NiAl shows absorption bands at $\approx$ 1.5 - 2 eV, 2.5 eV, 4.0 eV and 5.1 eV, while the CoAl, CoGa and NiGa alloys had absorption bands at 4.0 eV and CoAl and NiGa also had an absorption band at 1-2 eV. The most prominent compositionally dependent absorption peak at 2.4 eV in NiAl was not present in the other three alloys. The 4.0 eV peak was common to all alloys and independent of composition, although the peak position varied slightly from one alloy system to the next. The optical spectra of NiAl has been interpreted in terms of a rigid band model energy scheme; the extension of this scheme to CoAl, CoGa, and NiGa is still under consideration. While the resistivity measurements on the three alloys are incomplete, it appears that the compositional variation tends to support the view of clustering of point defects as the composition departs from stoichiometry similar to that observed in NiAl.

PUBLICATIONS

"The Reflectance of the Intermetallic Compounds NiAl and CoAl," D. Kiewit, J. J. Rechtien and J. O. Brittain, J. Phys. Soc. Japan 21, 2380 (1966).

"Optical Constants of β′-NiAl," J. J. Rechtien, C. R. Kannewurf and J. O. Brittain, J. Appl. Phys. 38, 3045 (1967).

INVITED TALKS

"The Rainbow Metal," Materials Science Department Colloquium, Northwestern University, February (1967).

MICROWAVE INVESTIGATIONS OF SEMICONDUCTORS, SEMIMETALS AND MAGNETIC MATERIALS

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Objective

To measure, at microwave frequencies, the transport parameters of semiconductors and semimetals leading to a better understanding and utilization of solid state microwave devices.

Approach

A theoretical and experimental study of areas of solid state physics which have potentials for useful microwave devices. Current areas involve Helicon waves in III-V compounds and in tellurium doped bismuth at cryogenic temperatures, as well as the theoretical foundation for electromagnetic wave instabilities in drifted solid state plasmas. Additional areas concern semiconducting non-reciprocal devices and acoustic-spin wave interactions in yttrium iron garnet. The Helicon waves are studied by means of two microwave spectrometers, one at 10 GHz and the other at 24 GHz. The semiconducting non-reciprocal device study is carried out at 140 GHz at liquid nitrogen temperature. The acoustic-spin wave interaction is explored at 1.4 GHz at room temperature by pulsed transmission techniques.

Progress

The cavity spectrometer for study of III-V compounds has been completed and experiments are underway with InSb and GaAs. The sample holder, dewar, and bridge technique for the experimental investigation of tellurium doped bismuth has been assembled and is being checked out on Ge and InSb samples. The study of drifted plasma instabilities is showing some encouraging results in developing new criteria for instability which are easier to apply than the Bess and Briggs methods. A semiconducting non-reciprocal device operating at 140 GHz has been demonstrated, the results

published and this study terminated. The preliminary study of the acoustic-spin wave interaction has been completed, the results polished, and the study is being extended to parametric interactions.

PUBLICATIONS

"Apparatus for Microwave Measurement of Transport Parameters in Semiconductors," M. E. Brodwin and M. K. Parsons, Rev. Sci. Inst., 38, 79 (1967).

"Circulator Action at 140 GHz in a Semiconductor Loaded Waveguide Junction," M. E. Brodwin and S. Kahn, Trans. MTT-15, 9, 530 (1967).

THEORY OF THE FUNDAMENTAL PROPERTIES OF SOLIDS

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Objective

To investigate by theoretical methods the electronic properties of crystalline solids. A partial list of the topics includes: infrared, optical and ultraviolet spectra; photoelectric emission; energy band theory; electronic defects states; structural (point) defects; deformation potential theory and the electronic properties of crystals at high pressures; and electronic states of impurities.

Approach

With respect to the problem of electronic states of bulk crystals (which includes optical, photoelectric and high pressure phenomena) we normally employ a semi-empirical pseudopotential. This involves parametrization of the first principles theory by a few (~3) parameters. The entire energy band structure over a range ~10 eV, is then deduced and direct comparison with experiment made.

In the case of point defects we use a dynamical interaction model which has its origin in the ideas of linear screening theory. Atomic form factors for the pair interaction functions are found. These are adjusted slightly to give agreement with observed phonon dispersion curves and relaxation and formation energies deduced.

A Green's function approach is used to study the formation of virtual (resonant) states formed in the continuum of zero gap semiconductor with a donor or acceptor defect present.

Progress

The optical spectrum of Si and Ge have been calculated and explained at high pressures, and the change in atomic form factor deduced. A calculation of the relaxation pattern and energy of a vacancy defect in sodium metal has been performed with good results. A calculation for the formation of resonant states in a non-direct zero gap semiconductor has been performed. A calculation of the diamond band structure and its optical spectrum has been performed along with a new analysis of the fine details of the Si spectra. A first calculation for the optical spectrum of GaAs has been completed. A new study of the optical spectrum deeper

in the ultraviolet is nearly complete. This includes not only regions of the band structure never studied before but also important corrections to electron-electron and electron-phonon scattering mechanisms.

PUBLICATIONS

"Form Factors and Ultraviolet Spectra of Semiconductors at High Pressure," D. Brust and L. Liu, Phys. Rev. 154, 647 (1967).

"Theory of Impurity States in Zero-Gap Semiconductors," L. Liu and D. Brust, Phys. Rev. 157 (1967).

"Relaxation Effects Around Vacancies in Sodium Metal," W-M Shyu, F. G. Fumi and D. Brust, J. Phys. and Chem. of Sol., 28, 717 (1967).

"Electronic Spectra of Crystalline Germanium and Silicon," Selected Papers in Physics, 156 25 (1967). This is a reprint of a physical review article.

"Pseudopotential Calculation of ε_2 for the Zincblende Structure: GaAs," W. Saslow, T. K. Bergstreaser, M. L. Cohen and D. Brust, Sol. State Comm. J, 662 (1967).

INVITED TALKS

"Energy Bands and the Photoelectric Effect in Semiconductors," Argonne National Laboratory, November (1966).

"Theory of Defects," Gordon Conference on Metals, Meriden, New Hampshire, August (1967).

DIFFRACTION STUDIES OF MATERIALS

J. B. Cohen
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Ph.D. Thesis Research

T. Ericcson
Research Assistant

J. Stiglich
Ph.D. Thesis Research(joint with Professor D. Whitmore) (Completed)

M. Hayakawa
Ph.D. Thesis Research

Objective

X-ray studies of the atomic arrangements in alloys, concerned with the presence and nature of small deviations from randomness of an alloy, and what these mean in terms of local arrangements.

Approach

Diffuse scattering measurements on alloys yield information with which a computer tells us actual atomic arrangements in alloys with local order and clustering.

Progress

The principal investigator was on leave of absence until the end of June, 1967. Accordingly, activities on this project were at a minimum. Six papers on previous research have been initiated. Also, the data taken on Al-Cu is still being analyzed and Mr. Ericcson will return this winter from Sweden to complete the work on Fe-Mo. (His travel is being paid by the Swedish government.)

Our computer models have been extended to include 108,000 atoms in three dimensions, and the programs involved have been fully tested. It has also been shown that with small clusters, as well as for local order, the first few short-range-order parameters determine the cluster configuration.

Programs for analysis of diffuse scattering measured in a volume of reciprocal space have been written and tested. A vacuum attachment for the diffractometer has been built, using a Be hemispherical window. This equipment employs three independent axes of rotation and can, therefore, be used with single crystals or powders. Temperatures from 77°K to 1000°K are possible. Large single crystals of Al-Ag alloys have been grown relatively free of high-angle mosaic and data are being collected on the ordered G.P. zones in this sytem, for use with our computer programs for obtaining their internal structure.

It has been found that the vacancy concentration in NiO-CoO solid solutions has a dependence on partial pressure of O_2 similar to that for the diffusivity in this system.

PUBLICATIONS

"Local Atomic Arrangements Studied by X-ray Diffraction," Met. Soc., Vol. 36, Edited by J. B. Cohen and J. E. Hilliard, Gordon and Breach, New York (1966).

INVITED TALKS

"Local Atomic Arrangements in Metallic and Ceramic Alloys,"

a. Institut fur Allgemeine Metallkunde und Metallphysik, Technische Hochschule, Aachen, Germany, October (1966).

b. University of Surrey, Physics Department, England, October (1966).

c. General Electric Generating Board, Materials Division, Leatherhead, Surrey, England, November (1966).

d. Technische Hochschule, Delft, Holland, November (1966).

e. Institute of Metals, The Technion, Haifa, Israel, December (1966).

f. Metallurgy Department, Cambridge University, Cambridge, England, January (1967).

g. I.R.S.I.D., St. Germain-en-laye, France, February (1967).

h. Faculte de Sciences, Orsay, France, February (1967).

i. Crystallography Club, Birmingham, England, March (1967).

j. Metallurgy Department, University of Liverpool, March (1967).

k. Central Institute for Industrial Research, Oslo, Norway, May (1967).

l. Danish Metallurgical Society, Copenhagen, Denmark (at the Danish Technical University), May, (1967).

m. Wihuri Physical Laboratory, Turku University, Turku, Finland, May (1967).

n. Metallurgy Department, Royal Institute of Technology, Stockholm, Sweden, May (1967).

o. Imperial College of Science and Technology, Royal School of Mines, Department of Metallurgy, England, June (1967).

p. Department of Metallurgy, Oxford University, England, June (1967).

"Some Materials Research at Northwestern University,"

a. Atomic Energy Commission, Roskilde, Denmark, May (1967).

b. Department of Physical Metallurgy, Finland Institute of Technology, Helsinki (Otaniemi), May (1967).

EFFECTS OF THERMO-MECHANICAL TREATMENTS ON THE SUBSTRUCTURE IN METALS AND ALLOYS

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This research is supported primarily by the Office of Naval Research.

Objective

Studies of the effects of thermal and mechanical treatments on faulting, microstrains, subgrain size in metals and alloys.

Approach

Fourier analysis of x-ray line broadening.

Progress

Work on faulting in b.c.c. refractory materials on other than {211} planes has continued, because of the increasing importance of these materials in modern technology. Techniques have now been developed to separate the effects of faults on the usual slip planes {110}, {211} and {321} from the effects of strain.

In addition, it has been found possible to analyze successfully a diffraction pattern for particle size and microstrain with fewer peaks than has been heretofore possible. In particular, only first order peaks are required rather than two orders for each crystallographic direction as has been the past procedure; there is no appreciable loss of information. This should be particularly useful for deformed solids, thin films, etc., where texture often makes it difficult to record many peaks.

A method for correcting the area of diffraction peaks, and the first few Fourier coefficients has been devised. This method not only increases the precision of Fourier analysis, but also allows a simple correction to the area of a diffraction peak for overlap, poor background determination, etc. This method should prove useful in determination of volume fraction with x-rays.

PUBLICATIONS

"Substructure, Stored Energy and Properties of Shock-Loaded Copper," D. C. Brillhart, R. J. DeAngelis, A. G. Preban and P. Gordon, Trans. AIME, 239, 836 (1967).

"Examples of Application of Line Broadening," D. E. Mikkola and J. B. Cohen in Local Atomic Arrangements Studied by X-ray Diffraction, Met. Soc. Vol. 36, Gordon and Breach, New York, 1966.

"Evaluation from X-ray Diffraction Profiles of Fourier Coefficients and the Microstrain Distribution Function," R. J. DeAngelis, in Local Atomic Arrangements Studied by X-ray Diffraction, Met. Soc. Vol. 36, Gordon and Breach, New York, 1966.

INVITED TALKS

"Analysis of Line Broadening and Examples of Applications," X-ray Residual Stress Seminar, Vanderbilt University, Nashville, Tennessee, August (1967).

SPECIFIC HEATS OF HIGH POLYMERS

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J. Currie
Ph.D. Thesis Research

Objective

To measure and compare the specific heats of different samples of polystyrene, especially above the glass transition temperature and for different annealing conditions. Also to study exothermic heats due to recombination of allyl-type free radicals in irradiated polyethylene.

Approach

A considerably modified Perkin-Elmer DSC-1 differential scanning calorimeter is being used for the comparison of the specific heats of polystyrene in connection with a computer routine for the reduction of the data. In the case of the irradiated samples, films of polyethylene are irradiated at liquid nitrogen temperature in vacuum by an electron beam accelerator and after alkyl free radicals have disappeared at room temperature and below, thermal scanning curves on the samples are taken by means of the DSC-1.

Progress

About 30 samples of polystyrene from different sources and with different thermal treatments have been studied in the DSC-1. At the present time these data are being calculated, converted to specific heats, encraties (specific heats divided by the absolute temperature), and entropy and enthalpy increments. At the moment it appears that a real difference, about 5%, can be detected in the liquid range between the different samples. This difference is being investigated.

The irradiated samples of polyethylene show definite exothermic peaks in the DSC-1 curves which can be correlated with the decay of allyl type free radicals.

PUBLICATIONS

"Crystallinity from Thermal Measurements," M. Dole, J. Polymer Sci. C18, 57 (1967).

INVITED TALKS

"Calorimetric Studies of States and Transitions in High Polymers," San Francisco Science Symposium, October (1966).

"Characterization of Polymers by Specific Heat Measurements,"

a. Wayne State University Polymer Conference Series, May (1967).

b. E. I. du Pont de Nemours & Company, Thermal Methods Conference, May (1967).

c. International Business Machines Corporation, Seminar Series in Polymer Chemistry, June (1967).

RADIATION CROSSLINKING OF POLYETHYLENE

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Objective

To analyze mathematically the data for the insoluble fraction of polyethylene produced by gamma- or electron beam irradiation as a function of dose in terms of different molecular weight distributions and crosslinking G-values. To find exact crosslinking yields and to obtain material balance.

Approach

The equation of Wesslau for the molecular weight distribution in polyethylene was used in connection with the Saito-Inokuti equations for production of gel as a function of dose and number of crosslinks per initial number average molecule. The resulting complicated expressions were solved by means of computer routines.

Progress

This work has been brought to a very successful completion. It has been shown for the first time (1) that crosslinking G-values increase with the dose; (2) that the temperature coefficient of crosslinking at zero dose is practically nil, but positive at higher doses; (3) that material balance exact to ± 0.1 G-unit has been realized at 35 and 120°C; and (4) that the initial slope of the Charlesby-Pinner solubility versus dose relation is a sensitive function of the initial molecular weight distribution.

PUBLICATIONS

"Theory of Gel-Dose Curves for Polymers Undergoing Simultaneous Crosslinking and Scission," O. Saito, H. Y. Kang and M. Dole, J. Chem. Phys. 46, 3607 (1967).

INVITED TALKS

"Computer Solution of Sol-Gel Relations," American Chemical Society, Miami Meeting, April (1967).

DEVELOPMENT OF A MACROMASS SPECTROMETER

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Ph.D. Thesis Research

This research is supported by the National Institutes of Health.

Objective

To develop a mass spectrometer for the macromass range and to attempt to produce intact macroions in the gas phase.

Approach

Very dilute solutions, 0.01 wt.% or less, of a polymer such as polystyrene of molecular weight 410,000 in a volatile solvent such as a mixture of three parts of benzene to two parts of acetone are being electrosprayed from a hypodermic needle charged negatively to about 10 KV into a nitrogen gas atmosphere. The gas mixture is sampled by a Bendix supersonic probe and the resulting ion current measured in a Faraday cage. It is planned eventually to study the ions in a Bendix time-of-flight mass spectrometer suitably modified for high mass ranges.

Progress

First results have been promising in that currents to the Faraday cage are about 10-fold greater in the case of the dilute polymer solution than in the case of the pure solvent.

This work is being done with the collaboration of the scientists of the Bendix Molecular Physics Research Laboratory, Detroit, Michigan.

PUBLICATIONS

"Plans for a Macromass Spectrometer," International Symposium on Macromolecular Chemistry, Tokyo, Japan, September 30, 1966. Preprint 6, 132 (1966).

THE RADIATION CHEMISTRY OF HIGH POLYMERS

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H. Y. Kang
Postdoctoral Research Associate

M. Budzol
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This research is supported by the U. S. Atomic Energy Commission.

Objective

To study reactive intermediates and other chemical groups produced in high polymers, especially polyethylene, by high energy radiations. To determine the temperature coefficient of the rate of crosslinking of chemical yields, and of chain scission during the radiation of polyethylene.

Approach

An irradiation cell has been designed so that thin films of the polymer can be irradiated with high speed electrons in vacuum at liquid nitrogen temperature and the ultraviolet and infrared spectra taken also at liquid nitrogen temperature in vacuum. The decay of transient species can be followed spectrometrically as the films are warmed up to room temperature.

The crosslinking yields have been obtained from a mathematical analysis of gel-dose curves at different temperatures. The effect of annealing, air oxidation and extraction time on the amount of gel (insoluble polymer) has been studied.

Progress

The analysis of the experimental gel-dose curves has been completed by means of a new mathematical treatment. It has also been found that the polymer samples have to be carefully annealed to eliminate free radicals after the irradiation and before exposure to air in order to prevent oxidation and chain degradation from occurring.

The study of the uv absorption band at 258 mμ and the infrared band at 942 cm^{-1} has shown that after the irradiated polyethylene film has been heated to room temperature in vacuo, both bands decrease in intensity at the same rate. This is a strong indication that these absorption bands represent the same species.

By making the infrared absorption measurements at liquid nitrogen temperature the bands are greatly sharpened and bands due to polyenes as well as to polyenyl free radicals can be detected.

Further studies have been made of uv bands in irradiated polyethylene at 215 and 310 mμ. At this time, however, their assignment remains uncertain.

PUBLICATIONS

"Ultraviolet Spectroscopy of Irradiated Polyethylene," D. M. Bodily and M. Dole, J. Chem. Phys. 45, 1428 (1966).

"Radiation Chemistry of Polyethylene. VIII. Kinetics of Growth and Decay of Polyene and Polyenyl Free Radical Groups," D. M. Bodily and M. Dole, J. Chem. Phys. 45, 1433 (1966).

"The Radiation Chemistry of Polyethylene. IX. Temperature Coefficent of Crosslinking and Other Effects," H. Y. Kang, O. Saito and M. Dole, J. Amer. Chem. Soc., 89, 1980 (1967).

"The Ultraviolet Spectroscopy of Irradiated Polyethylene," M. Dole and G. G. A. Böhm, in "Radiation Research", North Holland Publishing Company, Amsterdam, 1967, pp. 274-287.

"Reactive Intermediates in the Radiation Chemistry of Polyethylene," M. Dole and D. M. Bodily, Advances in Chemistry 66, 31 (1967).

INVITED TALKS

"Effect of Temperature on Radiation Crosslinking of Polyethylene," Japan Atomic Industrial Forum, Tokyo, Japan, September (1966).

"Ultraviolet Spectroscopy of Irradiated Polyethylene,"

a. University of California, Santa Barbara, October (1966).

b. Puerto Rico Nuclear Center, San Juan, Puerto Rico, March (1967).

"Ultraviolet and Infrared Spectra of Free Radicals and Transient Species in Irradiated Polyethylene," M. Dole and G. G. A. Böhm, Eighth International Symposium on Free Radicals, Novosibirsk, Siberia, July (1967).

DEPENDENCE OF STRESS ON ELASTIC CONSTANTS IN A COMPOSITE

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C. F. Hsieh
Ph.D. Thesis Research

Objective

To gain a better theoretical understanding of stresses induced in a fibrous composite material by surface loads.

Approach

Discovery was made through serendipity.

Progress

When the phases of a composite body are taken as isotropic, the stress induced by surface loads generally depends on three parameters formed from the elastic constants. As such one could take, for instance, the ratio of the shear moduli and the two Poisson's ratios. An important reduction in the dependence of stress on the elastic constants takes place, however, for fibrous or laminated composites. Under transverse loads, the stress in such composites can be shown to depend on only two parameters. The results can be expected to be useful in analytical and experimental work on composites.

PUBLICATIONS

"Effect of Elastic Constants on Stress in a Composite under Plane Deformation," J. Dundurs, J. Composite Mater., 1, 310 (1967).

EDGE DISLOCATION NEAR AN INCLUSION WITH SLIPPING INTERFACE

J. Dundurs
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A. C. Gangadharan
Ph.D. Thesis Research

Objective

To analyze mathematically the elastic interaction between an edge dislocation and an inclusion with a slipping interface, and to contrast the results with those for an adhering interface.

Approach

The problem is idealized by considering a circular inclusion, and treating the interaction by means of plane elasticity.

Progress

An important discovery has been that the force on the dislocation depends essentially on two parameters formed from the elastic constraints of the phases. This makes the interaction much more tractable in the elastic constants. The results show that the interaction with a slipping interface is radically different from that of the adhering interface.

ELLIPSOIDAL INHOMOGENEITY

J. Dundurs
Professor, Department of Civil Engineering

G. P. Sendeckyj
Ph.D. Thesis Research (completed)

Objective

To solve and interpret mathematically the disturbance introduced by an ellipsoidal inhomogeneity in a strain field with gradients.

Approach

The method of Green's functions employed by Eshelby for the uniform strain field was used also for the present problem.

Progress

The elastic solution for a linearly varying strain field that is disturbed by an ellipsoidal inhomogeneity has been obtained. The general solution contains a large number of special cases that are of interest. The interpretation of some of these has been completed, but the work on the majority is still in progress.

INTERACTION OF DISLOCATIONS WITH INHOMOGENEITIES IN PRESENCE OF APPLIED STRESSES

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R. Nuismer
M.S. Thesis Research

G. P. Sendeckyj
Ph.D. Thesis Research (completed)

Objective

To analyze theoretically the elastic interaction of dislocations with inhomogeneities in presence of applied stresses.

Approach

In order to make the problem tractable, the inhomogeneity is taken as a circular inclusion, and the interaction analyzed in two dimensions.

Progress

Previous work has been extended by including also screw dislocations, and the results prescribed in terms of interaction energy. A reconsideration of the edge dislocation also has yielded some new results. Thus, it has been shown that there are six essentially different types of behavior, depending on the elastic constants of the two phases. The results are far too complicated, however, for a more detailed summary.

INVITED TALKS

"Behavior of Dislocation in Presence of Inhomogeneities," Lehigh University, February 28, 1967, and Virginia Polytechnic Institute, March 2, 1967.

"Interaction of Dislocations with Inhomogeneities in Presence of Applied Stresses," Washington University, July 18, 1967.

FREE CARRIER REFLECTIVITY OF GRAY TIN SINGLE CRYSTALS

A. W. Ewald
Professor, Department of Physics

R. J. Wagner
Ph.D. Thesis Research

Objective

To evaluate band parameters through free carrier reflectivity measurements.

Approach

To study the free carrier reflectivity of variously doped gray tin single crystals in the temperature range from 25 to 273°K and the wavelength range from 13 to 220 microns. Various techniques were used to obtain either the complete free carrier reflectivity structure or only the wavelength of the reflectivity minimum. Substitution of these results, supplemented by conductivity and Hall data, into theoretical expressions for the optical constants permitted the evaluation of carrier effective masses. The temperature dependence of the reflectivity minimum of lightly n-doped crystals was used to evaluate the energy separation of the L_6^+ and Γ_8^+ conduction bands and its temperature dependence.

Progress

Measurements on p-type samples ranging in hole concentration from 10^{17} to 3×10^{19} cm^{-3} yielded a Γ_8^+ hole effective mass of 0.26 m_e. Measurements on n-type samples in the 10^{17} cm^{-3} range yielded Γ_8^+ electron effective masses in good agreement with the more accurate Shubnikov-de Haas values. On the basis of the study of one heavily n-doped sample (3.5×10^{18} cm^{-3}), the L_6^+ electron effective mass has been estimated to be 0.13 m_e. The above mentioned temperature dependence data were fitted (for $T \geq 120°K$) with a three-band free carrier model consisting of L_6^+ and Γ_8^+ electrons and Γ_8^+ holes all obeying Fermi-Dirac statistics. As a result, an estimate of $E_g(T) = \Delta E - \beta T$ has been made where $E_g(T)$ is the energy gap between the L_6^+ and Γ_8^+ conduction band minima. This fitting procedure gave $\Delta E = 0.11 - 0.12$ eV and $\beta = 4.5 \pm 0.5$ eV/°K. The inability of the three-band model to fit the temperature dependence data for $T < 120°K$ as well as anomalies in the effective mass of lightly n-doped material have led to a calculation of the contribution to the dielectric constant, $\epsilon(\omega)$, and the conductivity, $\sigma(\omega)$, of transitions off $k = 0$ between Γ_8^+ valence and conduction bands. The results suggest that $\epsilon(\omega)$ in the infrared might be substantially altered depending upon the carrier concentrations in the Γ_8^+ valence and conduction bands.

SHUBNIKOV-DE HAAS EFFECT IN SB-DOPED GRAY TIN

A. W. Ewald
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B. L. Booth
Ph.D. Thesis Research

Objective

To observe an enhanced oscillatory magnetoresistance at high doping levels due to screening of the impurity ions by heavy electrons.

Approach

The temperature, magnetic field, and orientation dependences of the oscillatory amplitude were measured in samples ranging in impurity concentration from 8×10^{15} to 10^{19} Sb atoms per cm^3. The data were analyzed to find the Dingle temperature T_D (which measures the effect of ionized impurity scattering on the amplitude), the energy dependence of the light electron (Γ_8^+) effective mass, and the shape of the Fermi surface.

Progress

A precipitous drop in T_D, corresponding to a sharp increase in the amplitude, was found at a concentration of 5×10^{17} cm^{-3}. The concentration dependence of T_D is in good quantitative agreement with the theory of Robinson and Rodriquez. For electron concentrations less than 5×10^{17} the energy dependence of the light electron effective mass agrees with the predictions of Kane's theory for InSb appropriately modified for the inverted gray tin band structure. At higher electron concentrations the effective mass increases more rapidly than predicted. Analysis of the angular dependence of the effective mass and oscillatory period in terms of a mathematical model similar to that of Dresselhaus, Kip, and Kittel for the Ge valence bands yields a nearly spherical Fermi surface slightly distended in the $\langle 111 \rangle$ directions. Spin splitting of Landau levels was observed in all samples having a sufficiently low T_D ($T_D < 2.5°K$) and was used to evaluate an effective g-factor.

PUBLICATIONS

"Screening-enhanced Shubnikov-de Haas Oscillations in Sb-doped Gray Tin," B. L. Booth and A. W. Ewald, Phys. Rev. Letters, 18, 491 (1967).

TWO-BAND GALVANOMAGNETIC EFFECTS IN GRAY TIN

A. E. Ewald
Professor, Department of Physics

C. F. Lavine
Ph.D. Thesis Research

Objective

To study the temperature, magnetic field, and doping dependence of the conductivity and Hall coefficient in the light of the Groves-Paul band structure model.

Approach

A series of n-type, slowly transformed filaments was made having Sb donor concentrations, N_d, between 5×10^{16} and 2.5×10^{19} cm^{-3} accurately predetermined by the white tin-Sb alloy composition. By suitable choice of temperature and doping, conduction was limited to at most two bands so that the single band characteristics could be obtained using standard two-band theory.

Progress

The 4.2°K values of Hall number, n_H, number from oscillatory magnetoresistance period, n_o, low field magnetoresistance, and Γ_8^+ electron mobility, μ_o, all exhibit discontinuous behavior as a function of N_d at a critical concentration, $N_c \simeq 5 \times 10^{17}$ cm^{-3}. For $N_d > N_c$ the $\langle 111 \rangle$ minima begin to be populated; n_o and n_H become substantially less than N_d, and the screening length decreases abruptly, causing an enhancement of μ_o. The mobility is in good qualitative agreement with the screened ionized impurity scattering theory of Dingle and Brooks and Herring. The infinite field Hall coefficient, $R(\infty)$, determined by fitting $R(H)$ to the two-band model, gives the total electron concentration in good agreement with N_d. From these measurements and the associated Fermi levels determined by Booth, values of the energy separation of the two conduction bands, $E_g = 0.092$ eV, and the density-of-states effective mass of one $\langle 111 \rangle$ ellipsoid, $m_{1d} \leq 0.21\ m_e$, were obtained.

For lower donor concentrations the μ_o values of several investigators were compiled and fit to the above theory. Good agreement is obtained if a doping dependent dielectric constant, first discussed by Wagner, is employed.

At temperatures between 4.2 and 100°K samples having $2 \times 10^{17} \leq N_d \leq 2.5 \times 10^{18}$ cm^{-3} exhibit an increasing $R(0)$ with temperature due to thermal transfer of electrons from the $\langle 000 \rangle$ to the $\langle 111 \rangle$ minima. These data are consistent with the above energy separation and mass values. We are also able to show that $dE_g/dT \leq -4 \times 10^{-5}$ eV/°K.

For "pure" single crystal samples intrinsic behavior was observed down to below 10°K. Using the conductivity, Hall coefficient, low field magnetoresistance, and the intrinsic condition (n = p) we were able to separate the electron and hole contributions. The hole mobility follows exactly a $T^{-3/2}$ dependence down to 20°K and has an absolute value compatible with acoustic phonon scattering.

PIEZORESISTANCE AND PIEZO-HALL EFFECTS IN GRAY TIN

A. W. Ewald
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B. J. Roman
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To study the effects of uniaxial stress as a function of temperature on the electrical conductivity and low field Hall coefficient in the light of the Groves-Paul band structure model.

Approach

Oriented single crystals of lightly doped n-type gray tin are subjected to uniaxial compression up to 5 x 10^9 dynes/cm^2 at temperatures ranging from 1.3 to 100°K. The low field Hall coefficient is analyzed to find the thermal energy gap (E_{TG}) which is produced when the strain removes the degeneracy of the Γ_8^+ conduction and valence bands. Mobility data are examined for the effects of possible large strain-induced anisotropies of the bands near $\vec{k} = 0$.

Progress

The temperature dependence of the Hall coefficient for various stresses in the region of intrinsic conductivity clearly indicates the presence of a thermal energy gap. For compression along a [100] axis, the rate of increase of gap with stress ($dE_{TG}/d\chi$) is found to be 6.0 x 10^{-12} eV cm^2/dyne $\pm$ 20% for the purest samples. This agrees quite well with the observed splittings of the degenerate valence bands in other cubic materials if one takes the thermal energy gap to be about half the energy splitting at the zone center as has been predicted by Cardona. In the more heavily doped samples, 2 x $10^{15} < N_D < 10^{17}$ cm^{-3}, the creation of a gap increases the temperature range of extrinsic conductivity.

The Γ_8^+ electron mobility decreases appreciably with uniaxial stress at liquid helium temperatures, the rate of decrease increasing with the purity of the material. This effect may be attributable to a stress induced anisotropy in the conduction band which will increase the energy density of states for low energies and consequently lower the average electron energy. The lower electron energy will enhance the Coulomb scattering from ionized donors and reduce the mobility. Additional reduction of the mobility may be caused by a reduction of the dielectric constant with stress.

Non-ohmic effects have been observed in the purest samples ($N_D \sim 4 \times 10^{14}$ cm^{-3}) under stress at liquid helium temperatures. The current-voltage characteristics are qualitatively similar to those of InSb at about the same doping levels as reported by Putley and others. Furthermore, the effect of stress on the current-voltage characteristics of pure gray tin is quite similar to the effect of a weak magnetic field in InSb.

PRECIPITATION AND SOLID SOLUTION STUDIES IN METALS

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W. O. Gentry
Ph.D. Thesis Research

S. Lahiri
Ph.D. Thesis Research

A. Urakami
Ph.D. Thesis Research

Objective

To study precipitation, precipitation hardening and solid solution hardening in metals. To relate structure to physical and mechanical properties. To determine the nature of the precipitates and kinetics of the processes. To elucidate solid solution softening which occurs at low temperatures in BCC and HCP metals.

Systems and Alloys: Fe base Mo, Fe base Cu, Ni base Al, Fe base NiAl, Fe base NiTi, Mg base binary alloys, Ti base binary alloys.

Approach

Measure magnetic and mechanical properties to 4.2°K and study metallographic structure versus alloying and heat treatment.

Progress

(1) Precipitation and solid strengthening of Fe-6 at. % Mo, completed. Precipitation of Fe_2Mo at 550°C in Fe-6 at. % Mo results in a substantial increase in σ the room temperature yield stress by 14 Kg/mm^2. Using Orowan's theory for the force required to bend dislocations between particles a spacing of 1900 Å was computed; the measured spacing between particles was 1800 Å. There is also a drastic increase in the rate of work hardening; the initial $d\sigma/d\varepsilon$ increases from 150 to 1600 Kg/mm^2. The thermal component of the shear stress τ_T is not affected by the precipitate but it is affected by dissolved Mo. In fact, addition of 1.5 to 2 at. % Mo reduces τ_T with essentially no further change to 6 at. % dissolved Mo. At room temperature the yield stress increases essentially linearly with dissolved Mo but at 77°K due to the reduction in τ_T alloy softening first occurs. This is attributed to the effect of alloying on a reduction in the stress required for the dislocation to surmount the Peierls barrier. The effective activation enthalpy at high τ_T, that is low test temperature, for Fe-6 at. % Mo is smaller than for iron. This is interpreted in terms of Weertman's theory for "weak" attraction between solute atoms and dislocations.

(2) A magnetic study of precipitation in Ni base Al alloys. Changes in Curie temperature, θ_c, were used to study precipitation of Al during aging in 11.1 and 13.8 a/o Al alloys. θ_c of the matrix increases as the Al segregates or precipitates. Starting from a structure randomized by cold working, solution treating gave a small increase in θ_c indicating precipitation occurred during the quench. θ_c also increased during short time aging of heavily cold worked material at 100°C. In both it is suggested that Al segregates to structural defects.

On aging at 450°C the change in θ_c is half over in only a few minutes. Published electron microscope studies at higher temperatures have missed the initial stage. With the 13.8 a/o Al alloy as quenched and after short aging times the magnetization decreases rather slowly on heating showing that the matrix solid solution is inhomogeneous. The curve "sharpens" on long aging showing that the matrix has become more homogeneous. This may be related to spinodal decomposition or an initial diffuse precipitate matrix interface boundary.

(3) A small amount of alloy softening at 77°K was observed on dissolving 1.7% Cu in Fe. The effect is less than with Mo. The specimens were purified by wet H_2 and by H_2 refluxed with ZnH_2, the technique developed by Stein and Low. Precipitation of the Cu by aging for three hours at 475°C increases the temperature dependence of the flow stress of the alloy. The kinetics of precipitation was followed by measuring the Young's modulus versus aging time. There is only a small change during the initial hour at 475°C while the flow stress increases rapidly. This may be evidence that the first precipitate is coherent bcc Cu and, therefore, causes little change in modulus. It becomes incoherent fcc Cu at later times; the latter has been seen by electron microscopy.

(4) Apparatus for growing Mg alloy single crystals using the travelling molten zone technique has been constructed and successfully operated to give crystals of desired composition.

PUBLICATIONS

"Precipitation Strengthening of Fe-6 at. % Mo," A. Urakami, H. L. Marcus, M. Meshii and M. E. Fine, Trans. ASM, September, 1967.

INVITED TALKS

"Precipitation Studies in Fe-Base Alloys," Tokyo Institute of Technology, August 28, 1967.

"Precipitation Studies in Fe-Base Alloys," Hokkaido University, August 29, 1967.

"Precipitation Studies in Fe-Base Alloys," Kyoto University, August 31, 1967.

"Precipitation Studies in Fe-Base Alloys," Osaka University, September 1, 1967.

"Precipitation Studies in Fe-Mo Alloys and Related Steels," Winter AIME Meeting, Los Angeles, February, 1967.

TRANSFORMATION AND PRECIPITATION STUDIES IN CERAMICS

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D. L. Johnson
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Ph.D. Thesis Research (with Professor D. L. Johnson)

F. B. Koch
Ph.D. Thesis Research (completed; with Professor M. E. Fine)

A. Krawitz
Ph.D. Thesis Research (with Professor J. B. Cohen)

E. W. Kruse
Ph.D. Thesis Research (with Professor M. E. Fine)

M. Takahashi
Ph.D. Thesis Research (with Professor M. E. Fine)

K. N. Woods
Ph.D. Thesis Research (with Professor M. E. Fine)

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

Objective

Precipitation and clustering, while extensively studied and exploited in metals, have been examined comparatively infrequently in ceramic systems. These phenomena and the structure and properties of the parent and product phases are being studied. Particular attention is being given to the effects of precipitates on the mechanical and magnetic properties of ceramics containing precipitates.

Approach

Studies of the Fe-O, Mg-Fe-O, Al-Ti-O, Mg-Al-O and Al-Fe-O systems are underway. Structures are determined by diffraction and microscopy. Principally mechanical and magnetic properties are measured.

Progress

(1) Mg-Fe-O Solid Solutions

Magnetic studies have shown that Fe^{+2}, as well as Fe^{+3}, is clustered when dissolved in MgO, even in solutions with only 1.2 cation pct. Fe. This is detected from the deviation of M-H curves from the Langevin or Brillouin functions. Aging in an oxidizing environment increases the cluster size. With essentially only Fe^{2+} present, shifted hysteresis is observed at 2 or 4°K in specimens with 9 (or more) cation pct. Fe. The blocking temperature increases with Fe content, indicating an increase in particle size. Curves of the reciprocal of susceptibility versus temperature exhibit a change in slope near the Néel temperature for pure FeO. The magnitude of the change increases with Fe content.

Clustering has also been detected in the (Ni,Mg)O system.

(2) Superparamagnetic Magnesioferrite Precipitates in MgO

This system shows promise for application, as there is no hysteresis in its M-H curves. To date the best initial susceptibility achieved is 27.47×10^{-3} emu/g/Oe at room temperature in MgO containing 2 cation pct. Ni and 10 cation pct. Fe.

Comparing results of magnetic measurements and electron microscopy, it has been found that the precipitate in (Mg,Fe)O formed at 700°C and 800°C in air is $Mg_{1.2}Fe_{1.8}O_{3.9}$. The saturation magnetization is higher than that for the bulk spinel, and the occupation of tetrahedral sites (by Fe^{2+}) is lower.

(3) Effects of Magnesioferrite Precipitates on Mechanical Properties of (Mg,Fe)O

Particle sizes obtained from electron microscopy and from analysis of the superparamagnetic behavior of (Mg,Fe)O containing this precipitate were combined with previous measurements of the yield stress. In a sample containing 1 cation pct. Fe, heat-treated in air, the flow stress appears to be independent of particle size, for sizes from 40 to 90 Å, but then decreases as the particles coarsen further. The strengthening appears to be due to creation of stacking faults when dislocations traverse a precipitate particle. The fault energy is computed to be 450 ergs/cm^2. With a sample containing 5 cation pct. Fe aged in air to its maximum strength, the fracture strength in flexure is three times that in pure MgO, but specimens show no evidence of ductility. The load to fracture with a 130° diamond pyramid indenter is the same as for pure MgO, or lower, indicating a low notch sensitivity. However, with large particles (in the micron range), the load is twice that for pure MgO, indicating a much improved notch sensitivity.

(4) Al_2O_3 - Ti

Specimens with precipitates have been prepared by sintering and aging pressed powders. These show strengthening over pure Al_2O_3, as did single crystals. The needle-shaped precipitate found in single crystals has been found for Ti cation percentages from 0.25 to 2.6.

(5) Fe_xO

The vacancy clusters reported by us to exist in quenched specimens, were found also at temperature in the one-phase field. The long-range periodic spacing of these clusters is destroyed, but there is still short-range order among them. As the ideal composition is approached, or as the temperature is raised, the clusters tend to disappear. There was no indication in the x-ray study of any other phase fields within the commonly accepted one-phase region.

PUBLICATIONS

"Strengthening of Sapphire by Precipitates Containing Titanium," S. E. Hsu, W. Kobes and M. E. Fine, J. Am. Cer. Soc., 50, 149 (1967).

"Magnetic Properties of Fe_xO as Related to the Defect Structure, F. B. Koch and M. E. Fine, J. Appl. Phys., 38, 1470 (1967).

"Superparamagnetic Magnesioferrite Precipitates from Dilute Solutions of Iron in MgO," G. P. Wirtz and M. E. Fine, J. Appl. Phys., 38, (1967).

"Precipitation Strengthening of Some Metallic Oxides," M. E. Fine, Int. Conf. on the Strength of Metals and Alloys, Japan Institute of Metals Conf. Preprints, p. 344 (1967).

INVITED TALKS

"Precipitation Studies in Ceramics, Purdue University, February 9, 1967.

"Precipitation Studies in Ceramics," New York Metals Science Club, March 2, 1967.

"Precipitation Studies in Ceramics," Case Institute of Technology, March 14, 1967.

"Precipitation Studies in Ceramics," Bendix Corporation, Materials Seminar, April 12, 1967.

"Precipitation Studies in Ceramics," University of Notre Dame, May 3, 1967.

HIGH TEMPERATURE MATERIALS

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Ph.D. Thesis Research

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T. Kennedy
Ph.D. Thesis Research (NDEA support)

R. Nygren
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J. Osborne
M.S. Thesis Research

J. Redmond
Ph.D. Thesis Research

Objective

To elucidate and study the relationships between structure and properties of cobalt base alloys.

Approach

Standard x-ray diffraction techniques combined with optical metallography have been used for phase identification purposes in the Co-W, Co-Mo, and Co-Cr binary systems and the Co-WC ternary system. Dilatometry and quantitative x-ray diffraction have been utilized to follow the kinetics of the allotropic transformation of f.c.c. cobalt to h.c.p. cobalt. In addition, further tests of the applicability of the quantitative x-ray diffraction technique derived for the Co-base alloy studies are being carried out by examining the effects of preferred orientation and grain size on the complete diffraction pattern.

Progress

The allotropic phase transformation of the cobalt matrix in the binary Co-W, Co-Mo and Co-Cr systems has been observed to behave in a manner similar to the previously reported transformation in the Co-WC system. However, the kinetics of the transformation are found to be orders of magnitude more rapid than in the Co-WC system. The actual matrix transformation follows a C-curve behavior similar to plain carbon

steels, with regards to the kinetics versus transformation temperature. For example, in the Co-20 wt % Cr alloy the transformation from an f.c.c. matrix to h.c.p. occurs in approximately 10 secs. at 600°C, while in the Co-WC system the transformation is only 70% complete at the end of 32 days for an equivalent temperature.

The transformation itself has proved useful in that by cycling through the transformation temperature the grain size can be refined by at least an order of magnitude (i.e., from 400 μ to 40 μ for a Co-35 wt % W alloy).

Finally, the possibility of using a least squares analysis for the quantitative x-ray diffraction method in place of the iterative technique previously reported, does not appear feasible, since the errors in measured intensity due to preferred orientation and grain size effects are not random.

INVITED TALKS

"Quantitative X-ray Diffraction," Department of Metallurgical Engineering, Illinois Institute of Technology, Spring 1967.

STRUCTURE AND PROPERTIES OF INTERMETALLIC COMPOUNDS

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E. Kraft
Ph.D. Thesis Research

D. Larson
Ph.D. Thesis Research

R. Sauer
Ph.D. Thesis Research

This research is supported by the Office of Naval Research.

Objective

To determine relationships governing ductility in intermetallic compounds.

Approach

Deformation has been induced in the cobalt silicides and in compounds having a nickel arsenide structure by means of a microhardness indentor. Both single and large grained polycrystalline material has been examined. X-ray diffraction and optical metallography techniques have been used to identify the resulting deformation markings.

Progress

Slip has been identified as the primary mode of deformation in the cubic compounds $CoSi_2$ and CoSi. In both compounds the slip plane has been identified as the {100} type. For the compound CoSi, the exact slip direction in a {100} plane has to be specified since this structure does not have four fold symmetry normal to the {100} planes.

In the case of the orthorhombic compound Co_2Si, deformation has been observed to occur both by twinning and by slip with the former being the more predominant mode. Twinning planes observed thus far are: {011}, {013}, and {210}.

NiSb, FeSb and CoSb compounds with the nickel arsenide structure have been prepared and preliminary deformation studies have been carried out. Deformation markings around indentations in NiSb have been identified as slip traces of the $\{10\bar{1}1\}$ slip plane. In the case of FeSb and CoSb no traces have been observed as yet. However, the predominance and severity of cracking around the indentation increases in these compounds in the order NiSb, CoSb and FeSb. This result is similar to

the previously reported increase in brittle behavior for the CsCl, TiX compounds whereX is Ni, Co, or Fe.

INVITED TALKS

"The Relative Ductilities of TiNi, TiCo and TiFe," Presented at "Symposium on TiNi and Associated Compounds," held at Naval Ordnance Laboratory, March 1967.

"The Deformation Modes of the Cobalt Silicides," Presented at International Symposium on Anisotropy in Single Crystal Refractory Compounds at Dayton, Ohio, June 1967.

THE DENSITY OF ELECTRONIC STATES IN "GAPLESS" SUPERCONDUCTORS

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J. E. Wilson
Ph.D. Thesis Research

Objective

To study the density of electronic states in "gapless" superconductors using the tunnel effect.

Approach

The Al/Al_2O_3 metal type tunnel junction is being studied. From the slope of the current-voltage curve the density of states of the superconducting metal is being calculated. Superconductors which display no resistance to current flow yet have no energy gap (sometimes just a depression in the density of states near E_f indicating states in the gap) are called "gapless" superconductors.

Progress

A cryostat contained in an ultrahigh vacuum has been built. With this cryostat quench deposited films are being produced and tested. The Pb/Al system turned out to be a type of gapless superconductor. Bismuth may also be a gapless superconductor when quench deposited on a 4°K substrate. In this cryostat at cryogenic temperatures tunnel sandwiches can be formed which are never exposed to temperatures higher than 4°K.

THE INITIAL OXIDE FORMATION ON A NICKEL FILM

R. Frerichs
Professor, Department of Electrical Engineering

R. K. Smeltzer
M.S. Thesis Research

Objective

Study of the initial oxide formation on nickel films by using the tunnel effect.

Approach

Incorporating the oxide in a tunnel sandwich and measuring the tunnel resistance as a function of the oxidation conditions.

Progress

The work for a Master's thesis: "Study of Initial Oxide Formation by Electron Tunneling" has been completed. In this work nickel films were "ac" sputtered on glass substrates and then oxidized under closely controlled conditions to produce oxide layers of the order of a few tens of Angstrom units. A tunnel structure is subsequently formed by evaporating a (superconductive) metal layer over the oxide. Measurements of the tunnel resistance under various conditions were made. It has been found possible to distinguish with this method between oxide layers whose effective thickness differs only by a few Angstrom units. Tunnel currents at liquid nitrogen and helium temperatures have been measured in order to get rid of possible ohmic conductivity through the semiconducting nickel oxide.

THE PROXIMITY EFFECT OF NIOBIUM

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C. J. Kircher
Ph.D. Thesis Research

Objective

To study the interaction of hard superconductors (niobium) with normal metals (copper) and with ferromagnetic metals (nickel).

Approach

Measuring the critical temperature of sandwiches consisting of hard superconductors and the other meta. The sandwiches are made by sputtering. The substrate temperatures are raised for the niobium layer in order to get crystalline structure and subsequently lowered before the deposition of the metal to avoid interdiffusion between the metal layer and the niobium layer.

Progress

This work has been brought to completion. Although the proximity effect has been previously examined for a number of "soft" metal superconductors, no work has been reported on the transition metal superconductors. Particularly interesting is the transition metal superconductor/magnetic metal in light of Matthias' interesting (albeit not too widely accepted) suggestion that superconductivity in the transition metals may be due to an electron pairing caused by magnetic interaction. The work has been completed recently and will be published.

X-RAY DIFFRACTION BY MULTILAYERED THIN-FILM STRUCTURES AND THEIR DIFFUSION

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J. B. Dinklage
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To make artificial layer structures for possible application as Bragg diffraction gratings for long wave-length x-rays.

Approach

The iron-magnesium system has been studied, as these two elements show only negligible interdiffusion. Structures of as many as 200 layers, providing layer spacings of 30-50 Å have been made by alternate evaporation in high vacuum.

Progress

The work has been successfully terminated. Persistent structures can be made using these two elements, Fe and Mg, which do not show any change due to interdiffusion. They compare favorably with lead stearate soap films as diffractive media. The diffracting characteristics have been measured from 8.34 to 23.7 A (Al-K_α to O-K_α). Within the temperature range 23-100°C an effective interdiffusion constant was determined. Details can be taken from the publication listed below.

PUBLICATIONS

"X-ray Diffraction by Multilayered Thin-Film Structures and Their Diffusion," J. B. Dinklage, J. Appl. Phys. 38, 3781 (1967).

MOLECULAR WEIGHT DISTRIBUTION IN BRANCHED POLYMERS

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Objective

Branching reactions during free-radical polymerization lead to a broadening of the molecular weight distribution of the resulting polymer. Theories predicting the behavior of such polymers are expressed in terms of summations over all species in the system. The purpose of this work is to derive the distribution functions necessary to analyze several important properties of branched polymers.

Approach

A differential equation for the number of polymer molecules with r repeating units and b branch points can be written as a function of conversion from the relative rates of the elementary reactions which build up the chains. A similar equation can be written for the number of growing radicals with r repeating units and b branch points. These equations are coupled, and solution for any particular set of elementary reactions centers around the problem of separation. Power series solutions and orthogonal polynomial expansions in terms of the distribution moments are logical approaches to the problem.

Progress

A series solution was obtained for the distribution when the elementary reactions are propagation, monomer transfer, polymer transfer, and terminal double-bond polymerization. The three parameters characterizing these reactions in vinyl acetate polymerization have already been established from measurements of average molecular weight. Applications are planned to studies of intrinsic viscosity, radiation crosslinking and non-Newtonian flow behavior in branched polymers.

RADIATION BEHAVIOR OF POLYMERS

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K. Yonetani
Research Assistant

Objective

This work seeks to clarify the factors affecting crosslinking and chain scission in solid polymer systems during exposure to high energy radiation.

Approach

Samples of polymers with known structure and molecular weight distribution are cast into films and irradiated in a Cobalt-60 gamma source in vacuum. The changes in molecular weight in the pre-gel and the shape of the gel curve in the post-gel region are analyzed using equations from the theory of random crosslinking and chain scission. Deviations from these equations are used to detect preferential reactions, and these are correlated with the structure of the chains.

Progress

The post-gel behavior of polyvinyl acetate with branch points along the chain (up to approximately two branch points/molecule) does not obey the random theory. The deviations depend on branching density and are consistent with a very rapid preferential scission at about 25% of the branch points. Measurements in the pre-gel region substantiate the observations, since lightly branched samples obey the random theory, while more heavily branched samples deviate considerably. Copolymers of vinyl acetate with very small amounts of isopropenyl acetate (less than 1 part in 500) have been prepared to simulate the branching along the chain in polyvinyl acetate hemopolymer. Preliminary tests have indicated rather substantial effects due to the presence of co-monomer.

INVITED TALKS

"Radiation Crosslinking in Polymers," Archer-Daniels-Midland Laboratories, Minneapolis, Minnesota, February 23, 1967.

RHEOLOGY OF AMORPHOUS POLYMERS

W. W. Graessley
Associate Professor, Department of Chemical Engineering

L. Legal
M.S. Thesis Research (Completed) (NASA Trainee)

J. Prentice
M.S. Thesis Research (Completed)

This research is partially supported by the Petroleum Research Fund of the American Chemical Society.

Objective

This work aims to relate the viscous and elastic properties of polymers in steady shearing flow to molecular properties such as molecular weight, molecular weight distribution and chain branching.

Approach

Viscosity and normal-stress differences are measured over a very wide range of shear rates using a Weissenberg Rheogoniometer. Concentrated solutions of polymers (20% - 60% polymer) with accurately known structures and molecular weight distributions are used. Viscosity-shear rate master curves are constructed from measurements at different temperatures, concentrations and molecular weights. The shapes of the master curves are compared with those predicted theoretically from the molecular weight distribution, and the relaxation times, zero-shear viscosities, and normal-stress coefficients are correlated with the appropriate molecular parameters.

Progress

Measurements on linear polystyrene of various molecular weight distribution have shown excellent agreement with theoretical calculations of the viscosity master curve. The relaxation time evaluated from the viscosity behavior of any solution was found to be almost identical to the relaxation time obtained independently from the normal-stress behavior, and both were close to the calculated Rouse relaxation time of the solution. The ratio τ (theoretical)/τ (experimental) differed from one solut to another, but was found to be an accurate linear function of the product ϕM, where ϕ is the volume fraction of polymer in the solution and M is the polymer molecular weight. Similar measurements on branched polyvinyl acetate have shown that viscosity decreases with branching. The near equality of relaxation times from viscous and normal-stress behavior is unaffected however, as is the agreement between these experimental relaxation times and the Rouse value.

PUBLICATIONS

"The Shear Rate Dependence of Viscosity in Concentrated Solutions of Polystyrene," W. W. Graessley, R. Hazleton and L. Lindeman, Trans. Soc. Rheology, 11 (1967).

"Viscosity of Entangling Polydisperse Polymers," W. W. Graessley, J. Chem. Physics 47 (1967).

INVITED TALKS

"Molecular Aspects of Polymer Rheology," Tennessee-Eastman Chemical Company, Kingsport, Tennessee, October (1966).

"Molecular Aspects of Polymer Rheology," University of California, Berkeley, California, February (1967).

STRUCTURE AND PROPERTIES OF BRANCHED POLYMERS

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R. Hartung
M.S. Thesis Research (NSF Fellow)

K. Nagasubramanian
Ph.D. Thesis Research (NSF and Phillips Fellow)

This research is primarily supported by the National Science Foundation.

Objective

Branching occurs in free-radical polymerization by the reaction between growing chains and repeating units on chains formed earlier in the process. Branching has a profound effect on mechanical properties, not only because of the structure, but also because it broadens the distribution of molecular weights in the system. The objectives of this work are to elucidate the effect of branching on distribution and to develop methods for quantitatively measuring branching density in polymer systems.

Approach

The leading moments of the molecular weight distribution can be expressed in terms of the rate constants for branching, chain transfer and propagation. The number-average and weight-average molecular weights M_n and M_w can thus be predicted as functions of conversion, and the rate constants can be evaluated by fitting experimental values of M_n and M_w. Branch densities (average number of branch points per molecule) can then be calculated at each extent of conversion, and compared with values obtained by other methods such as intrinsic viscosity studies. Measurements for different polymerization temperatures furnish activation energies for the rate constants, allowing one in principle to predict distribution and branching densities for a wide variety of polymerization methods and conditions.

Progress

Vinyl acetate polymerization in bulk at 60°C and 72°C furnished samples with M_n and M_w values that varied smoothly with conversion. Appropriate analysis furnished all the parameters necessary to define the structure and distribution of each sample. The calculated branching densities were in reasonable agreement with values inferred from intrinsic

viscosity measurements, but the results show that more theoretical work is needed on the interpretation of intrinsic viscosity in terms of structures for polydisperse systems.

PUBLICATIONS

"The Intrinsic Viscosity of Polydisperse Branched Polymers," W. W. Graessley and H. M. Mittelhauser, J. Polymer Sci. 2A, 5, 431 (1967).

INVITED TALKS

"Branching and Molecular Weight Distribution in Free Radical Polymers," Dow Chemical Company, Midland, Michigan, March (1966).

"Determination of Branching in Polymers," Airlie House Conference on Characterization of Macromolecular Structures (NAS-NRC), Airlie, Virginia, April (1967).

KINETICS AND PHASE TRANSFORMATIONS

J. E. Hilliard
Professor, Department of Materials Science and Science Engineering

D. Erb
Ph.D. Thesis Research

E. Philofsky
Ph.D. Thesis Research

Objective

(1) Determination of the effect of coherency strains on the interdiffusion coefficient. (2) Study of the decomposition of evaporated metastable alloys.

Approach

(1) Specimens of Cu-Pd containing short wavelength (~ 10 Å) coherent composition modulations are being prepared by evaporation. From X-ray diffraction measurements of the decay of the modulation after annealing, it is possible to determine very small interdiffusion coefficients ($< 10^{-30}$ cm^2 sec^{-1}). Depending on the type of substrate, specimens with either ⟨100⟩ or ⟨111⟩ textures can be obtained. The difference in the diffusion coefficients in these two directions are then compared with a theoretical prediction of the effect of coherency strains on diffusion.

(2) Highly supersaturated Cu-Ag and Aℓ-Ag alloy films are being produced by the simultaneous evaporation of the two components. The decomposition of these films is being followed by high- and small-angle X-ray diffraction.

Progress

Low temperature diffusivities in the ⟨111⟩ directions for Cu-Pd have been measured; it has so far been difficult to get reliable values for the ⟨100⟩ directions because of a tendency for the film to peal away from the substrate during annealing. Methods of solving the latter problem are presently being studied.

It has been found that the decomposition of the metastable Cu-Ag foils is primarily by cellular precipitation nucleated at the grain boundaries.

PUBLICATIONS

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

"A Theoretical and Analogue Study of Diffraction from One-Dimensional Modulated Structures," D. DeFontaine, in Local Atomic Arrangements Studied by X-ray Diffraction (Ed. J. B. Cohen and J. E. Hilliard) Gordon and Breach, New York, 1966.

INVITED TALKS

Some of the ARPA supported work was described in the talks on "Spinodal Decomposition" listed at end of Army Office of Research report.

QUANTITATIVE DETERMINATION OF MICROSTRUCTURES

J. E. Hilliard
Professor, Departments of Materials Science and Science Engineering

E. Philofsky
Non-thesis Research

Objective

Finding means of specifying and estimating the three-dimensional properties of microstructures -- i.e., Quantitative Metallography or Stereology.

Approach

Use of geometrical probability and statistics.

Progress

(1) E. Philofsky in collaboration with J. E. Flinn (with the Argonne National Laboratory at the time this work was done) have applied a procedure developed earlier in this project to the analysis of the strain distribution during the drawing of hollow metal tubes. This analysis has provided information not hitherto available. (2) A new method has been developed for determining the moments of the size distribution of convex particles from measurements on a section. (3) A new formula has been developed which facilitates the estimation of the number of particles per unit volume from measurements on a section.

PUBLICATIONS

"Applications of Quantitative Metallography in Recrystallization Studies," J. E. Hilliard, in Recrystallization, Grain Growth and Textures, ASM (1966).

INVITED TALKS

"Quantitative Metallography," ASM Grossman Memorial Lectures, Chicago, November 17, 1966.

"Determination of Structural Anisotropy," Invited Keynote address, Second International Conference of Society of Stereology, Chicago, April 8-14, 1967.

"Direct Determination of the Moments of Particle-Size Distribution," Second International Conference of Society of Stereology, Chicago, April 11, 1967.

SPINODAL DECOMPOSITION

J. E. Hilliard
Professor, Departments of Materials Science and Science Engineering

M. Källström
Non-thesis Research

M. Yang
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To determine the mode of decomposition in an Aℓ-Ag alloy containing 20 at. pct. Ag.

Approach

The decomposition during isothermal annealing of quenched specimens was followed by small-angle X-ray scattering.

Progress

The change in the X-ray spectrum during annealing displayed two maxima in the amplification factor versus wavenumber curve. (According to Cahn's theory for the early stages of spinodal decomposition, there should be only a single maximum.) The second maximum is believed to be due to the very early stages of coarsening. Values of the interdiffusion coefficient and the gradient-energy coefficient computed from the low-wavenumber side of the amplification curve were of reasonable magnitude.

INVITED TALKS

Descriptions of this work were included in the talks listed under the research supported by the Army Office of Research.

EXPLORATORY BASIC RESEARCH IN PHYSICAL SCIENCES

J. E. Hilliard
Professor, Departments of Materials Science and Science Engineering

E. L. Huston
Ph.D. Thesis Research

K. B. Rundman
Ph.D. Thesis Research

This research is supported by the U. S. Army Research Office -- Durham.

Objective

(1) Critical evaluation of Cahn's theory of Spinodal Decomposition. (2) Extension of Theory. (3) Study of phase transformations and thermodynamics of alloys by pulse heating.

Approach

(1) Use of small-angle X-ray scattering to follow spinodal decomposition. (2) Theoretical and numerical analysis. (3) Use of capacitor discharge to get very high (10^7°C sec^{-1}) heating rates.

Progress

(1) A theoretical study has been completed in collaboration with H. E. Cook and D. deFontaine of diffusion on a discrete lattice. This treatment is applicable to the determination of the kinetics and morphology in the early stages of ordering. (2) Reliable specific heats for pure metal foils have been obtained in the pulse-heating experiments.

PUBLICATIONS

"Early Stages of Spinodal Decomposition in an Aluminum-Zinc Alloy," K. B. Rundman and J. E. Hilliard, Acta Met., 15, 1025 (1967).

"Reply to: 'On the Decomposition of an Aluminum-Zinc Alloy'," J. E. Hilliard and K. B. Rundman, Scripta Met., 1, 37 (1967).

INVITED TALKS

"Spinodal Decomposition," University of Virginia, November 21, 1966.

"Spinodal Decomposition," Illinois Institute of Technology, Chicago, December 1, 1966.

"Recent Work in Spinodal Decomposition," Army Office of Research, Durham, North Carolina, January 13, 1967.

"Some Recent Theoretical and Experimental Results in Spinodal Decomposition," Local Chapter AIME, Detroit, January 16, 1967.

"Spinodal Decomposition," Carnegie Institute of Technology, Pittsburgh, February 9, 1967.

"A Review of Theoretical and Experimental Work on Spinodal Decomposition," two-week seminar at University of Denver, June 19-30, 1967.

"Nucleation," contribution to Workshop at M.I.T., July 20, 1967.

NUCLEATION OF GOLD ON MICA

R. L. Hines
Professor, Department of Physics

W. Morris
Ph.D. Thesis Research

Objective

To measure the nucleation rate of gold on mica under clean conditions and if possible, determine the activation energies involved in the growth process.

Approach

The gold is evaporated from a gold wire in a vacuum of 10^{-8} Torr onto a freshly cleaved mica surface. The wire is positioned relative to the surface so that the relative flux of gold on the mica surface can be determined as a function of position on the mica surface. The mica is then thinned by cleaving it and the clusters of gold atoms are directly counted using the electron microscope.

Progress

Excellent curves of nucleation rate as a function of flux and temperature have been obtained which show that the nucleation rate depends on the square of the atom flux. Also, interesting electron microscope photographs have shown the existence of satellite clusters.

ULTRA THIN GOLD CRYSTALS

R. L. Hines
Professor, Department of Physics

Objective

To investigate the factors limiting the thickness of continuous films and to measure the properties of ultra thin crystals.

Approach

The gold is evaporated onto an intermediate silver layer on top of heated rocksalt. The films are floated off on the surface of water and the silver is then dissolved in dilute nitric acid. The films are then mounted on grids for observation in the electron microscope.

Progress

The thinnest films that have been mounted are estimated to be about three atoms thick. Films 200Å or thicker can be mounted on rings to give unsupported areas 3 mm in diameter. A computer calculation has been finished which gives the electron microscope bright field and dark field intensities of crystals from 1 to 10 atoms thick as a function of crystal orientation.

GOLD CRYSTAL GROWTH AT 80° K

R. L. Hines
Professor, Department of Physics

Objective

To investigate the growth of vacuum evaporated gold films on rocksalt at liquid nitrogen temperatures and to determine if continuous films can be formed for very thin deposits.

Approach

The gold is evaporated in a vacuum of 10^{-8} Torr onto a freshly cleaved rocksalt crystal held at a temperature of 80 to 475°K. The gold is immediately covered with a carbon film to prevent surface diffusion and the film is then stripped and examined in the electron microscope.

Progress

This work has been completed. It has been found that the thermal energy of the impinging gold atoms is sufficient to cause appreciably surface migration even though normal surface diffusion is absent. Thus it is not possible to form continuous very thin gold films merely by cooling the rocksalt.

PUBLICATIONS

"Growth of Thin Gold Films on Rocksalt from 80°K to 475°K," E. F. Wassermann and R. L. Hines, J. Appl. Phys. 38, 196 (1967).

"Observation of Gold Films on Thinned Rocksalt," R. L. Hines and E. F. Wassermann, J. Appl. Phys. 38, 412 (1967).

RADIATION EFFECTS OF ION BOMBARDMENT

R. L. Hines
Professor, Department of Physics

W. Krakow
Ph.D. Thesis Research

D. Weber
Ph.D. Thesis Research

This research is supported by the U. S. Atomic Energy Commission.

Objective

This project uses ion bombardment to investigate the ranges of 10 Kev atoms, the production and annealing of imperfections produced by the 10 Kev atoms, and the effect of the imperfections on the physical properties of materials.

Approach

The ranges of the 10 Kev ions are investigated by measuring the transmission of ions through thin crystal foils. The foils are mounted on a goniometer to obtain the variation in ion transmission as a function of crystallographic orientation of the foil with respect to the incident beam. The defects produced by the bombardment are examined with an electron microscope.

Progress

Critical angles for channeling have been measured as a function of energy. Preliminary results indicate that a single ion impact can produce an imperfection cluster that is visible in the electron microscope.

PUBLICATIONS

"Channeling of D^+ and He^+ Ions in Gold Crystals," C. J. Andreen and R. L. Hines, Phys. Rev. 151, 341 (1966).

"Critical Angles for Channeling of H^+, D^+ and He^+ Ions in Single Crystal Gold Films in the Energy Interval 1-17 Kev," C. J. Andreen and R. L. Hines, Physics Letters 24A, 118 (1967).

"Critical Angles for Channeling of 1 to 25 Kev H^+, D^+ and He^+ Ions in Gold Crystals," C. J. Andreen and R. L. Hines, Phys. Rev. 159, 285 (1967).

INVITED TALKS

"Transmission of 1-25 Kev Ions Through Crystal Foils," Atomic Collision Conference, Chalk River, Ontario, September (1967).

"Channeling of Ions in Crystals," Dow Chemical Company, Midland, Michigan, May (1967).

THEORETICAL STUDIES OF PROTON TRANSFER MECHANISMS IN HYDROGEN BONDED SOLIDS

G. L. Hofacker
Associate Professor, Department of Chemistry

R. Rosenstein
Ph.D. Thesis Research

Objective

Theoretical studies can lead to the understanding of various effects of protonic motion in hydrogen bonded solids. Of particular interest are interactions of hydrogen bonds with the lattice vibrations and with each other, leading to ferroelectric and-through defects-to protonic semiconductor properties, as in ice or KH_2PO_4. The dynamics of interacting hydrogen bonds and of defects in hydrogen bonded solids needs to be developed and the forces of interaction have to be calculated by quantum mechanical methods.

Approach

1) We seek 2-dimensional, quantum mechanical computer solutions for the 3-atomic system of a hydrogen bond, X-H---Y, allowing proton transfer to occur under the influence of the X---Y vibrations. 2) We study the self-trapping of a proton in a double well potential through interaction with the lattice vibrations, by applying Green's function techniques. 3) A two-body approximation is employed in order to calculate the shielded interactions between protons in different hydrogen bonds by perturbation theory. 4) A suitably tailored version of polaron theory is used to develop expressions for the mobil'ty of defects.

Progress

Work has been completed on prediction of the collective excitations in a one-dimensional hydrogen bonded ferroelectric. Their spectrum was calculated for the first time over the whole temperature range, including all significant interactions between hydrogen bonds.

The final version of our computer program is in progress. It will give matrix elements for solving the time-dependent Schrödinger equation by a perturbation procedure.

The excitations and the dynamics of a proton in a double well potential, coupled to a relaxing lattice, were calculated by an intricate perturbation technique. Diagonal parts of the interaction between proton and lattice are taken into account to infinite order.

Excess protons in ice, exhibiting an abnormally high mobility, can be treated successfully as small polarons. A band conductivity region and a region with a prevailing mechanism of thermal activation are found at low, respectively high, temperatures.

PUBLICATIONS

"Collective Excitations in Hydrogen Bonded Ferroelectrics," G. L. Hofacker and S. F. Fischer, International Journal of Quantum Chemistry, Slater Issue.

"Hydrogen Bonds in the Light of NMR Measurements," G. L. Hofacker and U. Hofacker, XIV Collogne Ampére, Proceedings.

INVITED TALKS

"Hydrogen Bonds in the Light of NMR Measurements," XIV Collogne Ampére Ljubljana, Jugoslavia, September, 1966.

"The Dynamics of Hydrogen Bonded Systems," EUCHEM International Conference on the Nature of Hydrogen Bonding, Elmau, Germany, April, 1967.

PROTON TRANSFER IN HYDROGEN BONDED STRUCTURES

G. L. Hofacker
Associate Professor, Department of Chemistry

S. Fischer
Postdoctoral Research Associate

J. Fang
Ph.D. Thesis Research

This research is supported by the National Institute of Health.

Objective

To understand the proton transfer between different molecules in aqueous solutions as well as the functioning of ionic transport systems found in organisms.

Approach

We try to deduce from our understanding of the proton mobility in ice some of the salient features of proton transfer in water structures and work out the essential differences. Ice is studied as the model of an ionic transport system.

Progress

From theoretical results on the excess proton mobility in ice we were able to relate structural relaxation times of the lattice and tunneling frequencies with actual proton transfer frequencies. The role of wagging vibrations and O---O vibrations can be clearly understood and conclusions could be drawn regarding proton transfer in water. A detailed model for this process was designed. The excitation energies of an H_3O^+ couplet in water were calculated and the experimental activation energy for proton transfer identified with a particular excitation of the excess proton system.

DYNAMIC POLARIZATION OF PROTONS IN CHEMICALLY DOPED POLYMERS AT LIQUID HELIUM TEMPERATURES

C. Hwang
Assistant Professor, Department of Physics

D. A. Hill
Ph.D. Thesis Research

Objective

To understand the process of dynamic polarization in plastics doped with chemical free-radicals.

Approach

(1) By observing the dependence of proton polarization in plastics as a function of concentration of doping free-radicals, static magnetic field and (2) by proposing a phenomenological model of spin-spin interaction, we try to correlate the observed results with calculations based on the proposed model.

Progress

(1) We found that a new effect in dynamic polarization heretofore unobserved is germane in the chemically doped polymers. (2) We also found satisfactory agreement between measurements and model-calculations. (3) Mr. D. A. Hill is in the process of writing his Ph.D. Thesis based on the work reported here.

PUBLICATIONS

"New Effect in Dynamic Polarization," C. F. Hwang and D. A. Hill, Phys. Rev. Letters 18, 110 (1967).

"The Use of Chemically Doped Polystyrene as a Polarized Proton Target Materials," C. F. Hwang, B. A. Hasher, D. A. Hill and F. Markley, Nuclear Instr. and Methods 51, 254 (1967).

"Phenomenological Model for the New Effect in Dynamic Polarization," C. F. Hwang and D. A. Hill, Phys. Rev. Letters 19, 1011 (1967).

STRUCTURAL STUDIES BY DIFFRACTION METHODS

J. A. Ibers
Professor, Department of Chemistry

R. Delaplane
Ph.D. Thesis Research

D. Hodgson
Ph.D. Thesis Research

L. Schroeder
Ph.D. Thesis Research

Objective

To learn more about the structure of the solid state and the nature of the potential for hydrogen bonding.

Approach

X-ray and neutron diffraction studies of single crystals leading to complete crystal and molecular structure determinations.

Progress

(1) The novel compound $CsBr.1/3H_3OHBr_2$ has been prepared and characterized. The compound contains both the bibromide and the hydronium ion. The Br-H-Br distance, the first to be determined, is 3.35 A. (2) X-ray and deutron diffraction results on normal and deuterated oxalic acid dihydrate have been compared and have provided valuable information on the disposition of bonding electrons and lone pairs of electrons. (3) Potential function calculations on chromous and cobaltous acids have provided some indications of the reasons for the dramatic changes in the infrared spectra of these compounds on deuteration. The model used involves the coupling of the antisymmetric and symmetric O-H-O stretching modes. (4) Progress has been made on the studies of some systems in which molecular nitrogen is bound to a transition metal.

PUBLICATIONS

"Direct Determination of the Effect of Isotopic Substitution on Bond Lengths in Solid Oxalic Acid Dihydrate," R. G. Delaplane and J. A. Ibers, J. Chem. Phys., 45, 3451 (1966).

Review of "Hydrogen Compounds of the Metallic Elements," by K. M. Mackay, J. A. Ibers, Science 155, 684 (1967).

INVITED TALKS

"Diffraction and Spectroscopic Studies of Hydrogen Bonded Systems," Presented at the following:

San Francisco Science Fair, San Francisco, October, 1966,
Euchem Conference on Hydrogen Bonding, Schloss Elmau, Germany, April, 1967,
N.S.F. Summer School, University of Minnesota, July, 1967,
Institute of Solid State Physics, University of Tokyo, Tokyo, Japan, September, 1967.

"Catalytic Implications of Diffraction Studies," Stanford Research Institute, October, 1966.

STRUCTURAL STUDIES OF FIVE-COORDINATE TRANSITION METAL COMPLEXES

J. A. Ibers
Professor, Department of Chemistry

D. Bright
Postdoctoral Research Associate

J. Enemark
Postdoctoral Research Associate

B. Coyle
Ph.D. Thesis Research

K. Raymond
Ph.D. Thesis Research

J. Stalick
Ph.D. Thesis Research

This research is supported primarily by the National Science Foundation.

Objective

To detect and define accurately five-coordinated transition metal complexes.

Approach

X-ray and neutron diffraction studies of single crystals leading to complete crystal and molecular structure determinations.

Progress

Considerable work is in progress on this project. Rather than detail all of it one example will be given: The crystal and molecular structure of the complex $(Cr(en)_3)(Ni(CN)_5\,1\text{-}1/2\ H_2O$ has been determined. The $Ni(CN)_5^{3-}$ ion, long believed to exist in solution, but only recently isolated, occurs in two forms in the crystal structure. One $Ni(CN)_5^{3-}$ ion is a nearly perfect tetragonal pyramid, while the other is a distorted trigonal bipyramid.

PUBLICATIONS

"Studies of Metal-Nitrogen Multiple Bonds. II. The Crystal and Molecular Structure of Nitridodichlorobis(triphenylphosphine)rhenium(V), $ReNCl_2(P(C_6H_5)_3)_2$," R. G. Doedens and J. A. Ibers, Inorg. Chem., 6, 204 (1967).

"The Molecular Structure of Nitrosyldicarbonylbis(triphenylphosphine)-manganese, $Mn(NO)(CO)_2(P(C_6H_5)_3)_2$," J. Enemark and J. Ibers, Inorg. Chem., 6, 1575 (1967).

"The Crystal and Molecular Structure of Trichlorosilyltetracarbonyl-cobalt, $Co(SiCl_3)(CO)_4$," W. T. Robinson and J. A. Ibers, Inorg. Chem., 6, 1208 (1967).

"An Unexpected Product in the Reaction of $PtHCl(P(C_2H_5)_3)_2$ with C_2F_4. The Structure of the $PtCl(CO)(P(C_2H_5)_3)_2^+$ Cation and Evidence for the Existence of the SiF_5^- Ion," H. C. Clark, P. Corfield, K. R. Dixon and J. A. Ibers, J. Am. Chem. Soc., 89, 3360 (1967).

INVITED TALKS

"Five Coordinate Transition Metal Complexes," Symposium on Stereochemistry, Nara, Japan, September, 1967.

STRUCTURES OF SYNTHETIC MOLECULAR OXYGEN CARRIERS AND RELATED COMPLEXES

J. A. Ibers
Professor, Department of Chemistry

P. W. R. Corfield
Postdoctoral Research Associate

J. McGinnety
Postdoctoral Research Associate

B. Davis
Ph.D. Thesis Research

N. Kime
Ph.D. Thesis Research

This work is supported primarily by the National Institutes of Health.

Objective

To prepare and determine the molecular structures of synthetic molecular oxygen carriers and related complexes and thereby deduce possible factors contributing toward the bonding of oxygen to transition metals.

Approach

Old and new synthetic routes to various complexes, followed by x-ray studies of single crystals leading to complete crystal and molecular structure determinations.

Progress

Considerable progress has been made in several areas: In studies of the systems $IrXY(CO)(P(C_6H_5)_3)_2$, where X is halogen, and Y is an added ligand, for example, O_2, C_2F_4, $C_2(CN)_4$, etc., we now have a direct correlation between the bond length in the Y ligand (e.g., the O-O or C-C) and the ease with which the ligands adds to the metal. For example, in the O_2 series, we now have bond lengths of 1.30, 1.51, and 1.65 A for three different systems, and these changes correlate well with increasing strength of bonding of the oxygen to the metal. An accurate structure determination of the compound with $Y = C_2(CN)_4$ and X = Br has provided additional insight into the manner of bonding. The tetracyanoethylene group is no longer planar as a ligand, and the bonding seems best described as between sp^2 and sp^3 hybridization. The C-C distance is surprisingly long, 1.51 A, compared with 1.34 A in uncoordinated $C_2(CN)_4$.

PUBLICATIONS

Perspectives in Structural Chemistry, Vol. 1, J. D. Dunitz and J. A. Ibers (Editors), John Wiley and Sons, New York (1967).

"Studies of Metal-Nitrogen Multiple Bonds. I. The Crystal and Molecular Structure of Nitridodichlorotris (Diethylphenylphosphine) Rhenium(V), $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$, P. Corfield, R. J. Doedens and J. A. Ibers, Inorg. Chem. 6, 197 (1967).

"Structural Aspects of Reversible Molecular Oxygen Uptake," J. McGinnety, R. J. Doedens and J. A. Ibers, Science 155, 709 (1967).

"Some Advantages of a Complete Data Set," J. A. Ibers, Acta Cryst. 22, 604 (1967).

"Crystal Structure of cis-$Pt(P(CH_3)_3)_2Cl_2$, G. G. Messmer, E. L. Amma and J. A. Ibers, Inorg. Chem. 6, 725 (1967).

"The Crystal and Molecular Structure of U-Hydrido-U-Diphenylphosphidobis (Tetracarbonylmanganese), $(CO)_4Mn(H)(P(C_6H_5)_2)Mn(CO)_4$, R. J. Doedens, V. T. Robinson and J. A. Ibers, J. Am. Chem. Soc. 89, 4323 (1967).

INVITED TALKS

"Hydrogen, Oxygen and Nitrogen Complexes of Transition Metals,

(a) University of Washington, Seattle, October (1966).

(b) University of California, Irvine, October (1966).

(c) University of California, Riverside, October (1966).

(d) University of Western Ontario, London, Ontario, Canada, January (1967).

(e) University of Waterloo, Waterloo, Ontario, Canada, January (1967).

(f) University of Iowa, Iowa City, February (1967).

(g) E. I. du Pont Company, Wilmington, Delaware, May (1967).

(h) McGill University, Montreal, Canada, May (1967).

"Conference on Hydrogen, Oxygen and Nitrogen Complexes of Transition Metals," Osaka, Japan, September (1967).

EXPERIMENTAL AND THEORETICAL SINTERING STUDIES

D. L. Johnson
Associate Professor, Department of Materials Science

L. Berrin
Ph.D. Thesis Research (Completed)

H. Shingu
Ph.D. Thesis Research (Completed)

J. S. Smart, III
Ph.D. Thesis Research

D. Moore
M.S. Thesis Research (WPM Fellow)

The principal objective is to study the mechanisms of material transport in the sintering of ceramics and metals, and how these mechanisms are influenced by minor additives and atmospheric environment. Once the underlying principles are understood, attempts will be made to predict sintering behavior and to optimize the process. Most recently a much improved technique for calculating volume, grain boundary and surface diffusion coefficients from sintering data has been developed.

Approach

Isothermal measurements of shrinkage, shrinkage rate, and the diameter of the neck between particles are made as a function of time on compacts of closely sized spherical particles. With this information, the model previously developed in this laboratory can be utilized to compute the volume, grain boundary and surface diffusion coefficients.

Progress

Preliminary data for alpha iron have resulted in calculated diffusion coefficients for each of these mechanisms which are in close agreement with the values reported in the literature. The importance of grain boundaries in the sintering shrinkage of iron compacts was demonstrated. It was shown that a large fraction of the grain boundaries leave the interparticle necks as the alpha-gamma transition occurs, resulting in a drastic decrease in the shrinkage rate. High purity hematite was shown to sinter by grain boundary and surface diffusion.

Computer programs have been written which can synthesize sintering curves according to our model for various combinations of diffusion coefficients. The synthesized data for iron, based on the volume, grain boundary, and surface diffusion coefficients calculated from our data are in extremely close agreement with the experimental data.

GRAIN BOUNDARY SLIDING IN ALKALI HALIDES

D. L. Johnson
Associate Professor, Department of Materials Science

H. Sumka
Ph.D. Thesis Research

Objective

This study is designed to determine grain boundary shearing behavior of bicrystals of selected alkali halides as a function of temperature, orientation and purity.

Approach

The material will be zone refined in the purified halogen atmosphere and bicrystals will be pulled from the melt without exposure to the ambient atmosphere. It is hoped that by this technique the overall purity will be high, and in particular, that the hydroxyl content will be minimized. Grain boundary shearing will be observed directly and also measured with a recording strain gage.

Progress

The zone refiner-crystal puller apparatus and the testing apparatus are under construction.

SINTERING OF A DEFECT OXIDE

D. L. Johnson
Associate Professor, Department of Materials Science

P. Kumar
Ph.D. Thesis Research

This research is supported by the U. S. Army Research Office-Durham.

Objective

The effects of deviations from stoichiometry on the sintering behavior of cobaltous oxide will be studied. It should be possible to determine the mechanisms of material transport and whether Co or O ion diffusion is rate determining.

Approach

Compacts of closely sized spherical particles of CoO of controlled composition will be prepared. Isothermal measurements of shrinkage, shrinkage rate and neck size between particles will permit the determination of the mechanisms of material transport and the calculation of the appropriate diffusion coefficients. The dependence of these coefficients on deviations from stoichiometry will be studied.

Progress

A recording dilatometer and a gas train have been constructed and powder preparation techniques are being perfected.

ELECTRONIC PROPERTIES OF GERMANIUM ARSENIDE SEMICONDUCTORS

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

J. W. Rau
Ph.D. Thesis Research

Objective

To obtain information on the electronic band structure and other physical properties of Ge-As semiconducting compounds to evaluate the possible usefulness of these materials in semiconductor devices.

Approach

The compounds must be synthesized and single crystals grown. Physical measurements to be made will include optical absorption and reflectivity, electrical conductivity, Hall effect and magneto-resistivity. Because the materials are anisotropic, these will be made for as many crystllographic orientations as possible with the available crystals. Attempts will be made to dope the materials in a controlled manner.

Progress

Ingots of both GeAs and $GeAs_2$ have been synthesized, some containing relatively large single crystal sections. Vapor transport has produced small single crystals. The equilibrium arsenic pressure over the compounds has been found to be rather high which complicates growth of single crystals from the melt, though efforts to accomplish this are being continued. Preliminary optical measurements indicate that GeAs and $GeAs_2$ have a bandgap of approximately 0.8 eV. Electrical conductivity and Hall measurements have been made for certain crystallographic orientations on crystals cut from ingots.

ENERGY BAND CORRELATION FOR THE TERNARY THALLIUM-SULFUR-SELENIUM SYSTEM

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

R. S. Itoga
Ph.D. Thesis Research

Objective

The objective of this investigation is to study a noncubic semiconductor ternary system in order to learn and to understand the fundamental influences on the energy band structure and physical properties by changing the chalcogenide constituent.

Approach

By correlation of structural and dynamic information obtained by x-ray and optical techniques applied to the Tl-S and Tl-Se compound systems, the experimental results will be interpreted within existing solid state energy band theory. Measurements which will permit the determination of the conductivity, Hall and magnetoresistance tensor coefficients are planned.

Progress

From heating and cooling curves the phase diagram for the ternary system $TlS_xSe_{(1-x)}$ has been determined in part. Crystals of TlS, TlSe, and Tl_2SSe have been grown, and are being processed for optical measurements. The present results of the optical measurements indicate that TlS is birefringent and tests are in progress in order to determine whether it is dichroic also. Several structures for different crystallographic directions are evident in the reflectivity curves for TlS, and calculations to correlate the joint density of states function are being initiated.

PHYSICAL AND ELECTRONIC PROPERTIES OF ORGANIC COMPOUNDS

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

D. A. Miller
Ph.D. Thesis Research

Professor J. W. Kauffman of the Materials Science Department is co-advisor to this thesis project and the report of this work will be included in his annual technical report to ARPA.

OPTICAL ABSORPTION IN SILICON DISELENIDE

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

E. Hauschild
M.S. Thesis Research

Objective

In a continuation of the study of anisotropic RX_2 type semiconducting materials single crystals of silicon diselenide were prepared and investigated by optical measurements.

Approach

Vapor deposition techniques were employed to produce single crystals of $SiSe_2$. Growth orientation was determined by x-ray methods. Semiconducting properties were most easily determined by optical absorption and reflectivity measurements.

Progress

This work has now been completed. The chief results are as follows: (1) single crystal material of the Si-Se system can be prepared and preserved long enough to obtain physical measurements; (2) the growth morphology is somewhat unusual for orthorhombic crystal systems; (3) as a consequence of electrical resistivity and optical absorption measurements $SiSe_2$ can be classified as an insulating type semiconductor with an energy band gap of 1.73 electron volts. This is the first report of any such measurements on a C42 crystallographic type material. The chief problem in working with these materials is their extremely rapid chemical decomposition in ordinary laboratory atmosphere.

PROPERTIES OF THE SILICON ARSENIC SYSTEM

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

C. E. Miller
M.S. Thesis Research

Objective

To synthesize single crystals of the silicon-arsenic system and then to make electrical and optical measurements to determine the physical properties of this system. As a result of these measurements it is hoped to propose some details concerning the band configuration and the electronic transition mechanisms between bands.

Approach

Successful synthesis of crystalline material was carried out at temperatures in excess of 1100°C. The quality of composition versus reaction time has been studied to perfect the ingot material. This ingot material has been used to grow single crystals by chemical vapor transport with halogen gases.

Progress

Single crystal silicon arsenides have been synthesized as determined by x-ray diffraction measurements. Tentative crystal structure assignments agree with those reported in the literature. Needle-like single crystals have been grown and the effect of the temperature gradients and transporter conditions on the growth habit of these crystals is being studied. From preliminary optical measurements, it appears that the energy band gap will exceed one electron volt for SiAs.

SUPERCONDUCTIVITY IN THE γ-PHASE OF THE Tl-Te SYSTEM

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

K. Ishida
M.S. Thesis Research

Objective

To study the effect of carrier concentration and composition on superconductivity behavior in the neighborhood of stoichiometric composition for the γ-phase of the Tl-Te system.

Approach

Eight non-stoichiometric polycrystalline samples ranging 60.5% to 64.0% Tl have been prepared. Hall voltages and resistivities have been measured for each of these samples at 300°K, 77°K and 4.2°K respectively. The superconducting critical temperature, T_c, and critical magnetic field, H_c, have also been measured.

Progress

By x-ray methods it was confirmed that all eight compositions were within the γ-phase. Precise measurements of lattice constants by means of powder photographs showed no appreciable change in the lattice constants throughout the compositional range of the γ-phase. From the critical temperature composition curve it was observed that T_c has a maximum at the composition of 61.0% thallium and decreases toward both limits of the γ-phase range. The variation of T_c with carrier concentration was determined from Hall measurements; the highest T_c occurs at a carrier concentration of $1.1 \times 10^{21}/cm^3$. Additional measurements on the compositions: TlTe, TlTe (γ-phase + Tl) and 55.0% Tl(TlTe + γ-phase) are in progress.

PUBLICATIONS

(Completed Research Projects Not Previously Reported)

"Optical Absorption Coefficients of Vanadium Pentoxide Single Crystals," N. Kenny, C. R. Kannewurf and D. H. Whitmore, J. Phys. Chem. Solids, 27, 1237 (1966). This research was supported by the Air Force Office of Scientific Research and the Advanced Research Projects Agency of the Department of Defense.

"Optical Constants of β-Phase NiAl," J. J. Rechtien, C. R. Kannewurf and J. O. Brittain, J. Appl. Phys., 38, 3045 (1967). This research was supported by the Air Force Office of Scientific Research and the Advanced Research Projects Agency of the Department of Defense.

LASER MEASUREMENT OF SEMICONDUCTOR LIFETIME

C. R. Kannewurf
Associate Professor, Department of Electrical Engineering

M. E. Motamedi
M.S. Thesis Research

This research is supported by the Joint Services (Army, Navy and Air Force) Electronics Program.

Objective

The purpose of this research is to study a more accurate method for measuring semiconductor lifetimes. Also the application of this method for measuring the lifetime of high impurity semiconductors will be considered. Other methods generally employed are not applicable for this latter type of measurement.

Approach

A gallium arsenide injection pulsed laser with sufficient power and fast pulse risetime has been considered for generating a concentration of hole electron pairs at one point of the sample. Lifetime measurement is based on monitoring the decay of collected current by a wide band oscilloscope.

Progress

A compact high current and fast risetime pulse generator has been designed after selecting the appropriate laser diode that can produce necessary power. A special trigger circuit with variable repetition frequency was designed to control the power dissipation of the laser diode. A special dewar has been constructed to operate the diode laser at low temperatures.

DIFFRACTION STUDY OF ANOMALOUS TRANSITION IN PHENANTHRENE

J. W. Kauffman
Professor, Department of Materials Science

K-R Chiang
M.S. Thesis Research

Objective

Diffraction methods are used to study phenanthrene in order to elucidate the nature of the anomalies occurring in the neighborhood of 60°C.

Approach

Using powder phenanthrene, x-ray diffraction patterns will be taken from 20°C to 85°C to find the peak shifts. The lattice parameters will be determined from the peak positions at different temperatures. Neutron diffraction may be used to determine atomic positions in lattice.

Progress

The preliminary study was done by using Cu radiation on powder sample (Eastern Kodak) from 20°C to 80°C increasing 5°C each time. Tests were performed using Co radiation at room temperature also. We found different results from what the other groups did previously.

The new powder specimen holder and temperature controller are being prepared. We will try to take x-ray diffraction patterns from the high-purity sample from Brookhaven National Laboratory by using Co radiation or Cr radiation. Single crystals for x-ray diffraction and neutron diffraction studies will be obtained, if possible, in order to carry out such work.

PHYSICAL AND ELECTRONIC PROPERTIES OF ORGANIC COMPOUNDS

J. W. Kauffman
Professor, Department of Materials Science

D. A. Miller
Ph.D. Thesis Research

This research is in collaboration with Professor C. R. Kannewurf, Associate Professor, Department of Electrical Engineering.

Objective

To investigate the physical properties of certain organic compounds, with present emphasis on the variations of dielectric behavior and length dimensions with temperature.

Approach

The length changes and permittivity are measured on a GR 1615-A Capacitance Bridge as variations in 3-terminal capacitances. Attention is presently being given to phenanthrene because of interesting anomalies reported for the temperature dependencies of heat capacity and conductivity. Calibration will be made with respect to a quartz dummy specimen theoretical and experimental comparison will be made to anthracene, a structural isomer of phenanthrene (i.e., it has the same chemical formula, but a slightly different molecular structure), for which no such anomalies have been discovered.

Progress

Preliminary experiments have demonstrated the workability of the apparatus design, but have also indicated the need for refinements in several aspects. Chiefly they consist of considerably reducing the thermal response time of the apparatus themselves and producing greater stability and precision for measurement of capacitance changes to 10^{-5} pf. These refinements are now underway. Also, the capability of existing facilities is being extended through necessary purchases.

Researchers at Brookhaven National Laboratory have courteously provided high purity single crystals of anthracene and phenanthrene. If other compounds among the lower order polycyclic aromatic hydrocarbons are found to exhibit conductivity or heat capacity anomalies, as did phenanthrene, and if crystalline specimens of sufficient purity and size become available, investigations may be extended to these other compounds for a check on theory formulated for the phenanthrene-anthracene behavior.

PUBLICATIONS

(Completed research project not previously reported)

"Electron Irradiation of Al-1.7 at.% Cu in the Reverted Condition," H. Herman, M. E. Fine and J. W. Kauffman, J. Appl. Phys. 36, 1976 (1965).

INVITED TALKS

"Behavior of Point Defects in Metals," Natuurkundig Laboratorium, University of Amsterdam, August (1967).

"Recent Studies of Low Temperature Behavior of Point Defects in Electron Irradiated fcc Metals," Natuurkundig Laboratorium, University of Amsterdam, August (1967).

ELECTRICAL RESISTIVITY STUDIES OF THE RECOVERY OF POINT DEFECTS IN FCC METALS FOLLOWING ELECTRON IRRADIATION

J. W. Kauffman
Professor, Department of Materials Science

C. L. Snead, Jr.
Postdoctoral Research Associate

F. W. Wiffen
Ph.D. Thesis Research

This research is primarily supported by the U. S. Atomic Energy Commission.

Objective

The objective of this work is to study the low temperature behavior of the fcc metals following electron irradiation in order to obtain a model to explain the nature of the recovery of all fcc metals including the anomalous behavior such as occurs in gold. Finally, to relate this model to recovery occurring in the higher stages.

Approach

Specimens of copper, silver and gold were formed from approximately 120 cm of 5.1×10^{-3} diameter wire obtained from the Sigmund Cohn Corp. The wire was wound to give an irradiated length of nearly 70 cm. All starting material had a nominal purity of 99.999% and measured residual resistivities close to 4×10^{-9} ohm cm. Damage was introduced by 2.0 MeV electron irradiation at temperatures below 10°K. Resistance measurements by conventional potentiometric techniques were made at liquid helium temperature with a precision of $\pm 3 \times 10^{-14}$ ohm cm. Stage I damage recovery was followed by annealing the specimens isochronally with pulses of 20 min at temperatures 0.5°K apart. Pulse temperatures were measured using an NBS calibrated platinum resistance thermometer.

Progress

This research has now been completed.

We have examined the stage I recovery of electron irradiated copper, silver and gold and conclude that the behavior of all three can be explained by the same model. Stage I is due to the annihilation of interstitials at vacancies. Most of stage I is due to the collapse of close Frenkel pairs but a small amount of the end of stage I represents the random migration of interstitials to vacancies. Free interstitial migration is seen near 47°K in copper, near 31°K in silver and is suspected to occur at about 21°K in gold. The amount of recovery due to free interstitial recombination with vacancies decreases in the order copper to silver to gold. It has not yet been possible to positively identify a free migration process in gold.

The range of the interstitial interaction increases in going from copper to silver to gold. This makes impurity interstitial and interstitial-interstitial processes more important at the expense of interstitial-vacancy recombination. It is manifest in a decreasing I_E (free interstitial migration to vacancies) in going from copper to gold. The result is that in gold most interstitials are tied up before they can reach vacancy sinks. In silver and copper this competition for freely migrating interstitials results in less than 100% recovery in stage I. In copper where the free migration substage is large enough to be studied the recovery kinetics are complex, due to the three processes competing for the mobile interstitials. For any one of the three metals the competition between interstitial annihilation, dimer formation and impurity trappings results in a concentration dependence on the amount of stage I recovery.

PUBLICATIONS

"Stage I Recovery of Pure Silver and the Correspondence with Copper," F. W. Wiffen, C. L. Snead, Jr. and J. W. Kauffman, Phys. Letters 23, 22 (1966).

ELECTRON IRRADIATION DAMAGE IN THE REFRACTORY OXIDES

J. W. Kauffman
Professor, Department of Materials Science

J. Sickles
Ph.D. Thesis Research

This research is supported in part by the U. S. Atomic Energy Commission.

Objective

To investigate the relation of crystal bonding to radiation defect production in partially covalent bonded crystals.

Approach

Single crystal samples of MgO will be irradiated by a Van de Graaff electron accelerator over the temperature range of 4.2°K to 300°K. A dilatation experiment will be performed to determine the threshold energy and to study the annealing of defects produced at low temperatures. Optical absorption measurements will be made on irradiated samples at 77°K to verify results of the dilatation experiment, and to measure the effect of impurities on F-center production in MgO. Similar measurements will be made on Al_2O_3.

Progress

This project has only recently been initiated. Single crystal samples of MgO have been obtained. Apparatus for the dilatation experiment and the optical absorption experiment is currently being constructed.

POINT DEFECT CALCULATIONS

J. W. Kauffman
Professor, Department of Materials Science

M. A. Kirk, Jr.
Ph.D. Thesis Research

This research is supported by the U. S. Atomic Energy Commission.

Objective

To investigate the anisotropy of scattering, the configurational dependence, and the orientational dependence in the calculation of the resistivity of Frenkel defects in metals. To investigate simple models for determining expressions for the energy of migration of point defects, incorporating thermal vibration considerations.

Approach

The resistivity calculations will be based on the model due to L.C.R. Alfred and will incorporate improved semi-empirical phase shifts and the most recent calculations available for stable defect configurations, including lattice relaxations. The point defect migration calculations will be initially formulated in a three body Einstein model. This will hopefully be extended to a full lattice and values for vacancy diffusion, interstitial migration, and close pair Frenkel defect recombination energies will be calculated. Possible improvements to the model will be considered and incorporated where necessary.

Progress

This work is in the problem formulation stage. The advice and assistance from Dr. Alfred and Dr. Peter Sigmund, Argonne National Laboratory, is acknowle lged.

RADIATION ENHANCED DIFFUSION IN THE GOLD-SILVER SYSTEM

J. W. Kauffman
Professor, Department of Materials Science

D. Spreng
Ph.D. Thesis Research

This research is supported by the U. S. Atomic Energy Commission.

Objective

To measure radiation enhanced diffusion and relate this to defect production and migration in order to elucidate the nature of the various recovery stages, e.g., the nature of stage III recovery has not been established.

Approach

Thin films of modulated composition are prepared employing the techniques developed by Cook (H. E. Cook, Ph.D. Thesis, Department of Materials Science, Northwestern University). The films consist of several hundred alternate layers of high gold and high silver content. The thickness of the layers is varied from 7 A to 35 A. These samples are irradiated at approximately -150°C with a dose of 10^{18} electrons per square centimeter at an electron energy of 2 MeV. The decay of the composition fluctuation during annealing is observed both by x-ray and by resistivity methods.

This work is in collaboration with Professor J. E. Hilliard.

Progress

Preliminary experiments have shown that at room temperature the interdiffusion coefficient of the irradiated samples is less than 5×10^{-21} cm^2 sec^{-1}. A more precise experiment is being planned.

VOLUME CHANGE OF COPPER AND ALUMINUM AFTER ELECTRON IRRADIATION

J. W. Kauffman
Professor, Department of Materials Science

R. Hanada
Ph.D. Thesis Research

This research is supported in part by the U. S. Atomic Energy Commission.

Objective

The measurement of volume change of metals after particle irradiation gives information about the lattice relaxation around point defects.

Approach

In order to study volume change of Frenkel pair in F.C.C. metals, a highly sensitive dilatometer was constructed for low temperature (liquid He) electron irradiation. The sensitivity was 3×10^{-8} or 2 Å for a 6 mm specimen. The method is based on an accurate measurement of parallel plate capacitances which are formed between the top surface of specimen and vacuum evaporated thin gold film on a sapphire disk.

Progress

The length changes of Cu and Al were measured as a function of 2.2 MeV electron flux. The irradiation temperature was about 15°K. The lattice relaxation of a Frenkel pair thus obtained was + 1.3 atomic volume.

Subsequent isochronal annealing schedule (every 1°K with 10 min. holding time) showed clearly defined substructures which have not been observed by means of volume change measurements. The present annealing results are quite similar with those of resistivity measurements in both Al and Cu.

The physical significances of the present results are: (1) the lattice relaxation of an interstitial (positive) is much higher than a vacancy even in the case of a Frenkel pair; (2) either the lattice relaxation of a Frenkel pair does not depend on the distances between an interstitial and a vacancy or it depends on the distance in the same manner as resisitivity.

PUBLICATIONS

"Volume Change Recovery of Electron Irradiated Copper Below 60°K, J. W. Kauffman, Bull. Am. Phys. Soc. 2, 301 (1967).

"Length Change Measurements in Electron Irradiated Copper," J. W. Kauffman, Bull. Am. Phys. Soc. 11, 210 (1966).

ELECTRONIC PROPERTIES OF SEMICONDUCTORS

L. Liu
Associate Professor, Department of Physics

Objective

Theoretical study of the structure of the donor (acceptor) impurity states in a zero-gap semiconductor.

Approach

We work in the Wannier representation assuming a simple spherical and non-degenerate model for the conduction and valence bands making contact at the zone center. The impurity potential is assumed to be a statically screened Coulomb potential plus a central-cell potential which is localized at the site of the impurity ion. The coupled equations for the envelope functions of the impurity electron are solved by scattering formalism making use of the Coulomb Green's functions for the conduction and the valence bands. The expression for the phase shifts is then analyzed for the detailed structure of the impurity states.

Progress

This investigation has been completed within the framework of the simplified model stated in the above. Owing to the highly localized central-cell coupling, the s-states in the discrete hydrogenic spectrum are found to have been shifted in energy and broadened into resonant states. The equations for determining the positions and widths of these resonant states are derived. When both the intra-band and inter-band couplings are weak (as compared with the width of the bands), the results for the shift in energy and for the width of the impurity resonances become very simple and resemble those obtainable from perturbation theory and Born approximation respectively.

PUBLICATIONS

"Form Factors and Ultraviolet Spectra of Semiconductors at High Pressure," D. Brust and L. Liu, Phys. Rev. 154, 647 (1967).

"Theory of Impurity States in Zero-Gap Semiconductors," L. Liu and D. Brust, Phys. Rev. 157, 627 (1967).

DE HAAS - VAN ALPHEN STUDY OF FERMI SURFACE OF ANTIFERROMAGNETIC CHROMIUM

J. A. Marcus
Professor, Department of Physics

J. E. Graebner
Ph.D. Thesis Research

This research is also supported by the National Science Foundation.

Objective

To determine the Fermi surface of antiferromagnetic chromium.

Approach

By cooling high purity single crystals of chromium in magnetic fields ~33 kOe directed along [100] axes single domain states were prepared. The angular dependence of the multiple de Haas-van Alphen frequencies was recorded in digitized form using a Condon torsion balance. The data were computer analyzed to determine up to 20 simultaneously occurring de Haas-van Alphen frequencies.

Progress

Detailed data were obtained in five symmetry planes with frequencies ranging from 0.1 - 40 x 10^6 G. Ellipsoids and cylindrical surfaces were fitted to those families of data which could be followed through most of the symmetry planes. Many features of the data support the Fermi surface model resulting from a Mo-like surface modified by second order transitions as estimated by Falicov and Zuckerman.

PUBLICATIONS

(Not Previously Listed Publications Resulting from ARPA Supported Research Completed Prior to Report Period)

"Magnetic Breakdown in Zn and Its Alloys as Seen in the de Haas-van Alphen Effect," R. J. Higgins and J. A. Marcus, Phys. Rev. 161, 589 (1967).

"Weak Ferromagnetism in UO_2," P. D. Hambourger and J. A. Marcus, Phys. Rev. 157, 438 (1967).

MAGNETIC ANISOTROPY OF ANTIFERROMAGNETIC α-Mn SINGLE CRYSTALS

J. A. Marcus
Professor, Department of Physics

J. A. Oberteuffer
Ph.D. Thesis Research

This research is also supported by the National Science Foundation.

Objective

To grow single crystals of α-manganese and investigate their magnetic properties.

Approach

Small single crystals (5 mg) of α-Mn have been grown from high purity Mn by a vapor deposition method. The crystals are large enough to determine the temperature dependence of magnetic anisotropy using a Condon torsion balance.

Progress

Laue x-ray photographs show consistent single crystal reflection patterns on all sides and the symmetry axes of the four-fold magnetic anisotropy below the antiferromagnetic transition coincides with the crystal axes. The magnetic anisotropy shows a complicated temperature and magnetic field dependence which seems to indicate that there may be more than one antiferromagnetic structure below the Néel temperature (96°K ± 1°K).

SIZE DEPENDENT OSCILLATORY MAGNETORESISTANCE IN CADMIUM

J. A. Marcus
Professor, Department of Physics

P. D. Hambourger
Ph.D. Thesis Research

This research is also supported by the National Science Foundation.

Objective

To find some simpler metal in which to observe and study the oscillations originally discovered in Ga by Munarin and Marcus.

Approach

Tungsten, cadmium and zinc were selected as metals having appropriately shaped pieces of the Fermi surface for observation of the Munarin-Marcus size effect and which could be obtained in high purity single crystals of the appropriate orientations.

Progress

Despite the availability of exceptionally high purity (RRR = 60×10^3) single crystals of favorable size and shape, the effect has not been observed in tungsten so far.

In cadmium, using the field modulation technique, oscillations have been found with H in the (0001) and $(10\bar{1}0)$ planes. As in the case of Ga, the oscillations are distinguished from other size effect oscillations in that the amplitude increases to the highest fields used.

PUBLICATIONS

"Size Dependent Oscillatory Magnetoresistance in Cd," P. D. Hambourger and J. A. Marcus, Phys. Letters 25A, 461 (1967).

HIGH FIELD MAGNETORESISTANCE OF CHROMIUM

J. A. Marcus
Professor, Department of Physics

A. J. Arko
Ph.D. Thesis Research

This research is in collaboration with Dr. W. A. Reed, Bell Telephone Laboratories.

This research is supported by the National Science Foundation, the Air Force through the National Magnet Laboratories and by the Bell Telephone Laboratories.

Objective

To determine general topological features of the Fermi surface of antiferromagnetic chromium. To determine magnetic fields required to break down antiferromagnetic superlattice energy gaps. To investigate domain flipping behavior at high fields.

Approach

Single domain states were prepared by cooling high purity chromium single crystals through the Néel temperature in a field of 145 kOe. Measurements of the magnetoresistance, Hall voltage and transverse even voltage were made as functions of the direction and magnitude of magnetic fields up to 150 kOe. The angular dependence of magnetic breakdown oscillations was investigated in four high symmetry planes.

Progress

Evidence for magnetic breakdown of the superlattice energy gaps created by the antiferromagnetic spin-density wave was observed for all orientations of H. Two distinct regions of breakdown are evident: (1) a low field region with an estimated field $H_o < 30$ kOe which is believed to be breakdown of second order gaps, (2) a high field region with an estimated $H_o > 200$ kOe presumably resulting from first-order gap breakdown.

An anomalous negative longitudinal magnetoresistance was observed which is believed to be due to non-uniform current distribution resulting from the large anisotropy in megnetoresistance combined with non-ideal sample geometry.

PUBLICATIONS

"Magnetic Breakdown in Cr," A. J. Arko, J. A. Marcus and W. A. Reed, Phys. Letters 23, 617 (1966).

"High Field Magnetoresistance of Cr," A. J. Arko, J. A. Marcus and W. A. Reed, Proc. 10th Int. Conf. L. T. Physics, Moscow, Vol. 4 (Antiferromagnetism) (1967).

INVITED TALKS

"High Field Magnetoresistance of Cr," Symposium on Metals at Combined Meeting of the American, Canadian and Mexican Physical Soc., Toronto, June (1967.

MAGNETIC ANISOTROPY AND DOMAIN MODEL OF FIELD COOLED AF CHROMIUM

J. A. Marcus
Professor, Department of Physics

C. E. Burleson
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To modify existing domain models of chromium so as to include explicit temperature dependence of anisotropy and improved agreement with experiment.

Approach

To introduce explicit temperature dependence into Montalvo's domain model, to remove arbitrary assumptions from the domain model of Werner, et al and to obtain agreement between models and experiment.

Progress

Agreement between Montalvo's and Werner's models was obtained with satisfactory agreement with existing data.

DIRECT OBSERVATION OF LATTICE IMPERFECTIONS AND THEIR RELATION TO MECHANICAL AND PHYSICAL PROPERTIES

M. Meshii
Professor, Department of Materials Science

A. P. Brody
Ph.D. Thesis Research

K. Y. Chen
Ph.D. Thesis Research

J. A. McComb
Ph.D. Thesis Research (completed)

Objective

The objectives of this project are (1) to correlate the electron microscopic structures of metals with their mechanical and physical properties, (2) to interpret the structures in the atomic scale, and (3) to establish the atomic mechanisms leading to the formation of the structures.

Approach

Lattice-vacancy-related problems are being studied at the present time: (1) The basic properties of lattice vacancies, such as the energies of formation, migration and interaction, are studied using electrical resistivity and electron microscopy. The magnitude of interaction among vacancies is related to the clustering of vacancies, which can be studied electron microscopically. (2) The relation between the resulting electron microscopic structure and controlling parameter, such as the degree of supersaturation, temperature (or heat treatment for vacancy reactions), alloying elements and other imperfections such as dislocations, is critically examined. (3) Having established the structure, the relation of mechanical properties to the structure will be examined. The mechanical behavior of a material of a known structure is examined at various temperatures and strain rates and a possible mechanism of strength and plastic deformation is set up to explain the observation. The structure of the material after various degrees of plastic deformation is again examined with the electron microscope and the mechanism is examined with respect to the direct observation of the structure.

Progress

(1) The role of impurities in the nucleation of vacancy clusters was clarified. (2) The importance of the long range diffusion of vacancies in determining the final structure was recognized and a method of calculation including both the diffusion and the interaction of vacancies was established. (3) The direct correlation between optical

microstructures and electron microstructures by direct transmission and surface replication was established in quenched aluminum single crystals. (4) The importance of microstructural parameters in analyses of macroscopic deformation was established.

PUBLICATIONS

"Nucleation of Vacancy Clusters in Quenched Aluminum and Gold," M. Meshii, J. A. McComb, K. Y. Chen and T. H. Mori, The Nature of Small Clusters (1966), H.M.S.O. London, England, p. 84.

"Comments on a Recent Calculation of the Nucleation Rate of Vacancy Clusters," J. A. McComb and M. Meshii, J. of Applied Phys., 38, 2388 (1967).

"Precipitation Strengthening of Fe-6 at. % Mo," A. Urakami, H. L. Marcus, M. Meshii and M. E. Fine, Trans. A.S.M. 60, 344 (1967).

INVITED TALKS

"Morphology of Plastic Deformation and Dislocation Kinetics in Quenched Aluminum," M. Meshii, Colloquium, Department of Materials Science, Northwestern University (1967).

"Current Problems in Analysis of Plastic Deformation," M. Meshii, Seminar, Technical Research Laboratory, Kawasaki Steel Corp., Kobe, Japan (1967).

"Morphology of Plastic Deformation and Dislocation Kinetics," M. Meshii, Colliquium, Department of Metallurgy, Osaka University, Osaka, Japan (1967).

DIRECT OBSERVATION OF LATTICE IMPERFECTIONS AND THEIR RELATION TO MECHANICAL AND PHYSICAL PROPERTIES - GOLD BASE ALLOYS

M. Meshii
Professor, Department of Materials Science

M. Bapna
Ph.D. Thesis Research

M. Graham
M.S. Thesis Research

R. Herring
Ph.D. Thesis Research

J. Vander Sande
Ph.D. Thesis Research

This research is also supported by the National Institutes of Health.

Objective

(1) To establish the kinetics and morphology of precipitation in gold base alloys. (2) To study the plastic behavior of the alloys at various stages of precipitation. (3) To establish the ultimate strengthening-ability of this alloy system. (4) To examine the microplastic analysis of plastic deformation with specimens of known structure and to relate the macroscopic parameter to the atomic configuration and defect structure.

Approach

(1) Micro-hardness, resistivity and electron microscopy are employed to study the kinetics and morphology of precipitation. (2) Tensile tests and creep tests will be used to study the plasticity of single crystals of alloys whose structures are determined in section (1). (3) The mechanical response of single crystals will be examined as a function of temperature, strain rate, applied stress, initial structure, and the different stages of deformation. The relation between macroscopic parameters and microstructure is being critically examined. (4) Transmission electron microscopy will be used to examine structures of specimens at various stages of deformation. The findings will be correlated with the results of Section (3).

Progress

(1) Experimental study of precipitation hardening in iron-gold alloys has been completed and a report of the result is being prepared. The correlation between precipitation and corrosion in the alloy is currently being examined by a group in the Bio-Materials Department. (2) The

plastic behavior of gold solid solutions (currently Au-Zn) is being studied by the creep apparatus reported previously.

EFFECT OF POINT DEFECTS ON MECHANICAL PROPERTIES OF METALS

M. Meshii
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T. Mori
Postdoctoral Research Associate

M. Levin
M.S. Thesis Research

T. Mifune
Ph.D. Thesis Research

This research is supported by the Atomic Energy Commission.

Objective

The primary purpose of this project is to study the interaction between dislocations and point defects. This interaction also helps to identify point defects and to examine the nature of these point defects. Since the point defect-dislocation interaction is one of the simplest mechanisms involved in determining strength and plastic deformation, the present study is also used to examine critically the existing theories.

Approach

Electron irradiation at low temperatures is used as a means to generate a random distribution of interstitial atoms. Using single crystals of f.c.c. metals and alloys as specimens, the effects of the irradiation with various doses and of the subsequent annealing on the mechanical properties such as yield stress, work-hardening parameters, and temperature and strain rate dependencies of flow stress, are studied. The interpretation of the results can be facilitated by the information available for electron irradiation damage. At the same time, this information can be further confirmed or can be improved according to the results provided by the present study. The effects of lattice vacancies which are generated by rapid quenching are also included in the investigation.

Progress

(1) The effectiveness of electron irradiation in investigating the work-hardening of single crystals has been demonstrated. (2) The interaction energy between a dislocation and an interstitial was determined in copper and was found to be about half of that in aluminum. The width of the dislocation was proposed to be one of the variables

determining the interaction energy. (3) A new description of plastic deformation using microscopic parameters has been developed using the results obtained in quench-hardening aluminum.

PUBLICATIONS

"Electron Irradiation Hardening and the Interstitial Dislocation Interaction in Aluminum," K. Ono and M. Meshii, The Nature of Small Clusters, H.M.S.O. London, England, p. 539 (1966).

"Point Defect Hardening of Aluminum--II. Analysis of Electron Irradiation Experiments at 23°K," K. Ono and M. Meshii, Trans. A.S.M., 60, 426 (1967).

"Effect of Electron Irradiation of Plasticity of Metallic Single Crystals," K. Ono and M. Meshii, Proceedings of International Conference on Solid State Physics Research with Accelerators, Brookhaven National Laboratory (1967).

INVITED TALKS

"Electron Irradiation Strengthening in Metals and Alloys," M. Meshii, Colloquium, Division of Metallurgical Engineering, University of Washington, Seattle (1967).

"Electron Irradiation Strengthening in Metals and Alloys," M. Meshii, T. Mifune and K. Ono, International Conference on the Strength of Metals and Alloys, Tokyo, Japan (1967).

"Effect of Electron Irradiation on Plasticity of Metallic Single Crystals," K. Ono and M. Meshii, International Conference on Solid State Physics Research with Accelerators, Brookhaven National Laboratory, New York (1967).

CONTINUUM THEORY OF DISLOCATIONS AND PLASTICITY

T. Mura
Professor, Department of Civil Engineering

J. A. König
Postdoctoral Research Associate

Objective

To fill out a gap between classical continuum plasticity and dislocation theory. To interpret phenomenological and mathematical formulae in classical plasticity by terms of dislocation behavior and to yield a new direction of plasticity with more physical background.

Approach

Statistical and macroscopical mean of a dislocation distribution is given by a tensor form. Macroscopical stress fields in elasto-plastic materials are considered as the sum of dislocation stresses and applied elastic stresses. The Mises yield criterion under combined stress fields is treated as a statistical mean of Peach-Koehler's force.

Progress

This work considers the plane strain problem of a semi-infinite domain loaded by a semi-infinite band of uniform pressure on the surface. The proposed approach could predict not only the stress field but also the plastic strain field which could not be found by any classical method.

PUBLICATIONS

"Continuum Theory of Plasticity and Dislocations," T. Mura, Int. J. Eng. Sci. 5, 341 (1967).

INVITED TALKS

"Continuum Theory of Dislocations and Plasticity," International Union of Theoretical and Applied Mechanics Symposium, Stuttgart, Germany, September (1967).

"Generalized Stress Strain Laws Developed by Dislocation Theory," AIME Work Hardening Symposium, Chicago, November (1966).

STRESS FIELDS OF DISLOCATIONS

T. Mura
Professor, Department of Civil Engineering

D. R. J. Owen
Ph.D. Thesis Research (Completed)

Objective

To derive stress fields of dislocations whose shapes are frequently observed in electron-microscopy. To derive interaction energy between dislocations and interstitial impurities on vacancies.

Approach

The two methods have been extensively established by Mura during the last five years with ARPA support. One is Green's tensor method and the other is Fourier transformation method.

Progress

The first solution was found for the stress field of helical dislocation of uniform shape with the Burger's vector along its axis and applied to find the interaction energy with a point defect. We had also the solution to the problem of a Frank dislocation network near a free surface and calculated Peach-Koehler's force.

PUBLICATIONS

"Periodic Dislocation Distributions in a Half-Space," D. R. J. Owen and T. Mura, J. Appl. Phys. 38, 1999 (1967).

"Dislocation Configurations in Cylindrical Coordinates," D. R. J. Owen and T. Mura, J. Appl. Phys. 38, 2818 (1967).

DISLOCATION PILE-UP IN TWO-PHASE MATERIALS

T. Mura
Professor, Department of Civil Engineering

J. G. Kuang
Ph.D. Thesis Research

This research is supported primarily by the National Science Foundation.

Objective

To find distribution functions and total numbers of dislocations piled up against the interface of two-phase materials for given applied forces. The result has significant meaning for work-hardening theory and fracture criteria of composite materials.

Approach

Vanishing of a total Peach-Koehler's force leads to the integral equation which is solved exactly by using Wiener-Hopf technique with Mellin-transforms.

Progress

The first analytical solution was obtained for edge dislocation pile-up. Distribution curves of dislocations are shown for several combinations of material constants in the two phases when a uniform shear force is applied.

LIFETIME SPECTROMETRY

E. W. Schlag
Associate Professor, Department of Chemistry

H. Sandhu
Postdoctoral Research Associate

M. E. Starzak
Ph.D. Thesis Research

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

Objective

To decide on the feasability and construct a method of measuring lifetime of isolated molecules excited with light from a monochromator.

Approach

Modulate light at 30 MHz and measure the phase shift of the fluorescent signal as a function of excitation wavelength.

Progress

We have successfully made measurements employing our 30 MHz phase fluorimeter to measure the radiate lifetime of excited β-naphthylamine. Our original goal has been met, that is, to do lifetime spectrometry. To do this we had to (1) illuminate on a nanosecond time scale with monochromatic light of arbitrary wavelength, and (2) perform this measurement in the collisionless region, i.e., where collision events are relatively improbable compared to radiation. A lifetime here is defined only for the isolated vibronically excited state. More conventionally, at higher pressures, lifetimes of excited states can be determined, but only for the ground vibronic state. A continuous sweep of lifetimes versus excitation energy is then a direct probe of the nature of the excited potential surface.

By adding a small amount of an inert gas one can observe energy transfer effects by observing differential lifetimes. This concept has been tested with propylene as an inert gas. It gave an absolute value for the collision frequency for the particular vibronic state, as well as the average amount of excitation energy transferred in the first collision.

PUBLICATIONS

"Kinetische Analyse der Relaxation Lochangeregter Vielatomiger Molekile in der Gasphase durch Messung von Fluoreszenzlebensdauern," H. V. Weyssenhoff and E. W. Schlag, Kurzvorträge der physik. Chem. 1178 (1967).

"Absolute Measurement of Inelastic Collision Cross Sections for Vibronic Excited States," E. W. Schlag, H. v. Weyssenhoff and M. E. Starzak, J. Chem. Phys. 47, 1860 (1967).

INVITED TALKS

"Direct Measurement of Rate Constants for Excited States," E. W. Schlag, H. v. Weyssenhoff and M. E. Starzak, International Photochemistry Conference, Munich, Germany, September (1967).

"Energy Transfer Measurements in Excited States," H. v. Weyssenhoff, E. W. Schlag and M. E. Starzak, International Photochemistry Conference, Munich, Germany, September (1967).

Lecturer at the Conference on Gas Kinetics, University of California at Irvine, January (1967).

SOLID STATE PHYSICS STUDIES BY NUCLEAR MAGNETIC RESONANCE

D. S. Schreiber
Assistant Professor, Department of Physics

L. Shen
Postdoctoral Research Associate

J. P. Kopp
Ph.D. Thesis Research

R. Wade
M.S. Thesis Research

Objective

To determine some magnetic and electronic band structure parameters for some rare earth-hydrogen alloy systems.

Approach

By measuring the Knight shift, line shape and width and spin lattice relaxation time of the proton in the R.E. - H_x alloys as a function of temperature, magnetic field and hydrogen concentration x. In several special cases it is possible to also measure these nuclear magnetic resonance parameters for the rare earth ion nucleus.

Progress

Work on the steady state proton nuclear magnetic resonance in the light rare earth-hydrogen alloys (Ce-; Pr-; and Nd-) has just been completed. Treating these systems (which in some cases have higher electrical conductivities than the pure rare earth metal) using the simplified rigid band model with overlapping R.E. and H bands, we have concluded that there is a fractional occupation of the H 1s conduction band of 0.2 electrons/atom. We have also determined (for the first time) that Pr $H_{2.0}$ and Ce H_x, $2.0 < x \leq 2.5$ magnetically order at temperatures $T > 2.4°K$ where T_c depends on x. Activation energies for proton self diffusion have been determined as a function of x and for the different rare earths and are found to vary typically from 1 to 4 kcal/mole depending on x and the R.E. Steady state studies of the Pr^{141} nuclear resonance and the pulse spin lattice relaxation time measurements on the H' resonance are underway.

PUBLICATIONS

"Nuclear Magnetic Resonance Studies of Magnetic Properties of Light Rare Earth Hydrides," D. S. Schreiber and J. P. Kopp, J. Appl. Phys. 38, 1373 (1967).

"Proton Knight Shifts in the Light Rare Earth Hydrogen Systems," D. S. Schreiber and J. P. Kopp, Phys. Letters 24A, 323 (1967).

INVITED TALKS

"Hydrogen Alloys," Physics Seminar Series, University of Pittsburgh, January (1967).

MAGNETIC PROPERTIES OF METALS AND ALLOYS

D. S. Schreiber
Assistant Professor, Department of Physics

L. D. Graham
Ph.D. Thesis Research

J. A. Neumeier
Ph.D. Thesis Research

E. Von Meerwall
Ph.D. Thesis Research

This research is supported primarily by the National Science Foundation.

Objective

To determine some electronic and magnetic properties of magnetically dilute alloys using nuclear magnetic resonance techniques.

Approach

By observing the nuclear resonance of the non-magnetic host metal into which small amounts of normally magnetic transition metals (Fe, Co, Mn, etc.,) have been imbedded, we can measure the extent or absence of magnetization in the regions surrounding the magnetic impurity. Implicit in these measurements is the determination of some transition metal-conduction electron coupling constants.

Progress

Work on the systems of Fe and Co as dilute impurities (up to ~0.1% atomic percent) in platinum metal have been studied by observing the Pt^{195} nuclear resonance. By observing the Knight shift and linewidth (and line shape) of the platinum resonance we are able to describe the distribution of magnetization at relatively large distances (~20 or 30 Å) from the impurity. Measurements were made as a function of temperature, magnetic field and concentration (from 0.005 to 0.1% atomic of magnetic impurity). It was found that in addition to an oscillating (RKKY) polarization in the Pt host, that below $T \approx 3°K$ for Co in Pt an anomalous weakening of the impurity moment appeared to set in. Since this system is also one of the so called giant moment systems, this might at first sight appear unusual. Such behavior has, however, been observed in several other non-giant moment magnetic impurity systems and is believed to be related to what is now called the Kondo Effect. Similar studies are now just underway in a system which shows altogether different magnetic behavior (i.e., the vanishing of the moment at all reasonable temperatures) specifically the dilute Fe: Al system where we are observing the Al^{27} nuclear resonance.

PUBLICATIONS

"Conduction Electron Polarization in the Paramagnetic State of a Giant Moment Dilute Alloy," D. S. Schreiber and L. D. Graham, Phys. Rev. Letters 17, 650 (1966).

INVITED TALKS

"Local Moments in Platinum Metal," General Physics Colloquium, College of William and Mary, Williamsburg, Virginia, October (1967).

MÖSSBAUER EFFECT STUDIES OF MATERIALS

L. H. Schwartz
Associate Professor, Department of Materials Science

N. Abe
Ph.D. Thesis Research

H. Chow
Ph.D. Thesis Research

Objective

The Mössbauer effect is being used to investigate precipitation phenomena and magnetism in iron bearing alloys. Studies of Fe-Mo alloys have now been completed.

Approach

Thin foils of Fe-Mo, quenched and annealed for various times have been examined using a constant velocity Mössbauer spectrometer. Resolution of the change in the hyperfine spectrum with composition allowed a measurement of the concentration of Fe in the ferromagnetic solid solution and in the paramagnetic iron bearing precipitate.

Progress

The analysis of the precipitation data was completed and has been published. The composition dependence of the hyperfine splitting in the matrix has been explained. Mössbauer spectra for a series of alloys of closely spaced composition from 2.1 at.% Mo to 6.0 at.% Mo were examined. The hyperfine field and peak widths showed a composition dependence suggestive of overlap of the disturbed surroundings of impurity atoms in accord with results of neutron diffraction studies of dilute impurities in iron. Analysis of the Mössbauer data in conjunction with unpublished saturation magnetization measurements of A. Aldred led to the deduction of a fractional increase in average iron magnetic moment of 0.25 per atomic percent and a magnetic moment per Mo atom of $0.4\mu_B$ directed antiparallel to the iron moment, the latter value in good agreement with the neutron diffraction results.

PUBLICATIONS

"A Study of Precipitation in Stainless and Maraging Steel Using the Mössbauer Effect," H. L. Marcus, M. E. Fine and L. H. Schwartz, Trans. ASM 59, 468 (1966).

"The Mössbauer Spectra of FeMo Alloys," H. L. Marcus and L. H. Schwartz, Phys. Rev. 162, 259 (1967).

NEUTRON DIFFRACTION STUDIES OF MATERIALS

L. H. Schwartz
Associate Professor, Department of Materials Science

E. Hall
Ph.D. Thesis Research

M. Steinitz
Ph.D. Thesis Research

M. C. Yang
M.S. Thesis Research

Objective

To use neutron diffraction to study the changes in magnetic structure of materials induced by the application of hydrostatic pressure. Concurrently high pressure studies of the polymorphism in CuI were carried out.

Approach

The neutron diffraction studies are being made at the Argonne National Laboratory using a time-of-flight spectrometer constructed under the author's direction. Pressures up to 11 kbar are obtained in an aluminum alloy piston-cylinder device using CS_2 as the pressure transmission medium. The studies of CuI involved measurements of volume change using a piston cylinder apparatus as well as x-ray diffraction and optical properties using a diamond anvil pressure cell.

Progress

The equipment is now ready for the neutron diffraction experiments which will commence in November, 1967. This research will henceforth be supported by a grant from the National Science Foundation. The studies of CuI have been completed. Four triple points were found in the temperature-pressure range to 450°C and 20 kbar. It was concluded from the very small changes in volume, entropy, and compressibility between the α, β, γ, h_1 and h_2 phases in this system, that all are related by subtle changes in the (111) planar stacking sequence, a phenomenon known as polytypism.

MÖSSBAUER EFFECT STUDIES OF STEELS

L. H. Schwartz
Associate Professor, Department of Materials Science

D. Chandra
Ph.D. Thesis Research

This research is supported by a grant from the Inland Steel Foundation.

Objective

To use the Mössbauer effect in the studies of precipitation in iron based alloys with applications to the understanding of strengthening mechanisms in age-hardenable steels.

Approach

Earlier work in this laboratory and elsewhere has demonstrated that the Mössbauer effect can yield detailed information about the kinetics of precipitation and the composition of the matrix and precipitate. Paramagnetic precipitates are easily distinguished from the matrix by a characteristic single line pattern in the former case and a six-line pattern in the latter.

Progress

Work is beginning on a study of precipitation in the Fe-Ti and Fe-Cu systems. Alloys have been prepared and suitable specimen preparation techniques established. These studies will be supplemented by measurement of other property changes, such as Young's modulus, in collaboration with Professor M. E. Fine and his students.

NEUTRON DIFFRACTION STUDIES OF MATERIALS SUBJECTED TO HIGH PRESSURE

L. H. Schwartz
Associate Professor, Department of Materials Science

E. Hall
Ph.D. Thesis Research

M. Steinitz
Ph.D. Thesis Research

This research, initiated under support of ARPA, is now supported by the National Science Foundation.

Objective

To use neutron diffraction to study the changes in magnetic structure of materials induced by application of hydrostatic pressure.

Approach

The neutron diffraction studies are being made at the Argonne National Laboratory at the CP-5 reactor, using a time-of-flight spectrometer constructed under the author's direction. Pressures up to 11 kbar are obtained in an aluminum alloy piston-cylinder device using CS_2 as the pressure transmission medium. The pressure is monitored and controlled by feedback using a calibrated manganin resistance in the high pressure cylinder.

Progress

The time-of-flight spectrometer has been completed and high pressure experiments are now beginning. Studies will include alloys consisting of dilute additions of manganese to chromium to help clarify the nature of the antiferromagnetism in this element. A second experiment will deal with the magnetic structure of MnAs. Theoretical predictions suggest a change from ferromagnetism to antiferromagnetism in the pressure and temperature range accessible to this instrument.

SYNTHESIS AND STRUCTURES OF INORGANIC COMPOUNDS

D. F. Shriver
Associate Professor, Department of Chemistry

I. Wharf
Postdoctoral Research Associate

D. B. Brown
Ph.D. Thesis Research (NSF Fellow)

J. A. Dilts
Ph.D. Thesis Research

P. M. Kuznesof
Ph.D. Thesis Research (completed)

Objective

Principal: Synthesis and structure determination of unusual coordination compounds. (a) Vibrational spectroscopy of unusual inorganic species. (b) Factors affecting structures and bonding in Lewis acid-base complexes. (c) Structures of cyanide polymers.

Approach

(1) Infrared and laser Raman spectroscopy are being applied to the study of Lewis acids and bases. The resulting frequencies are fit by normal coordinate vibrational analysis.

The structures of cyanide polymers are investigated by means of infrared spectroscopy, Mössbauer spectroscopy (joint studies with Professor Lyle Schwartz), magnetic susceptibility, and X-ray powder diffraction.

(2) Pyrolysis products of simple boron-nitrogen compounds have been studied in joint studies with Professor F. E. Stafford. Molecular orbital calculations have been employed to interpret previously determined ionization potential data on borazine and its derivatives.

Progress

(1) Vibrational studies of the polyfunctional Lewis acids, $F_2BCH_2CH_2BF_2$ and $Cl_2BCH_2CH_2BCl_2$ have been completed. For the latter compound solid state spectra are interpreted in terms of an anti-conformer. In liquid and gas states acentric conformers exist. Judging from solid state infrared spectra $F_2BCH_2CH_2BF_2$ may have a less symmetric structure. This work is complete and has been submitted for publication.

A laser Raman unit has been assembled and is now in operation. It is being applied to the study of SnX_3^- salts (X = F, Cl, Br, I) for which a nearly complete set of infrared data has been obtained.

The compound $Fe_3[Cr(CN)_6]_2$, ferrous chromicyanide, undergoes a series of solid state reactions which involve the interchange of N-coordinated (N), interstitial (I), and C-coordinated (C) metal ions. In this description the original complex is $Fe_2(N)$, Fe(I), $Cr_2(C)$, which upon heating in the absence of air leads to an Fe-Cr interchange: $Fe_2(N)$, Cr(I), [Fe(C), Cr(C)]. Air oxidation of this compound produces a material of uncertain structure which may be reduced to $Cr_2(N)$, Fe(I), $Fe_2(C)$. A report on this work has been accepted for publication.

(2) Work on the pyrolysis of H_3NBH_3 has been completed. The results indicate that in the solid state this compound decomposes to give small quantities of H_2BNH_2. Papers on this work and on molecular orbital calculations for cyclic B-N compounds are in preparation.

PUBLICATIONS

"Electron Impact Ionization Potentials of Methyl Substituted Borazines," P. M. Kuznesof, F. E. Stafford and D. F. Shriver, J. Phys. Chem., 71, 1939 (1967).

"Ambident Nature of Cyanide," D. F. Shriver, Structure and Bonding, 1, 32 (1967).

"Bridge Addition Compounds," J. J. Rupp and D. F. Shriver, Inorg. Chem., 6, 755 (1967).

"Observation of the Chelate Effect with a Bidentate Lewis Acid," M. Biallas and D. F. Shriver, J. Am. Chem. Soc., 89, 1078 (1967).

"Complexes of Trichlorostannate(II) with Ib Metals," J. A. Dilts and M. P. Johnson, Inorg. Chem., 5, 2079 (1966).

LEWIS BASE PROPERTIES OF TRANSITION METALS

D. F. Shriver
Associate Professor, Department of Chemistry

J. F. Jackovitz
Postdoctoral Research Associate

G. Kubas
Ph.D. Thesis Research

R. Scott
Ph.D. Thesis Research (completed)

B. Swanson
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

Synthesis, relative stabilities and vibrational analysis of unusual Lewis salts.

Approach

(1) The titration of metal complexes with Lewis acids has been followed by cryoscopy, pressure changes, and visible and infrared spectroscopy.

(2) In other work the X-ray structures of $CH_3C{\equiv}NBX_3$ complexes are being investigated in collaboration with J. A. Ibers.

Progress

Complexes of $Ir(P(C_6H_5)_3)_2ClCO$ with a series of boron containing Lewis acids have been prepared. Metal-boron bonding is indicated.

PUBLICATIONS

"Bridge Addition Compounds," J. J. Rupp and D. F. Shriver, Inorg. Chem., 6, 755 (1967).

"Observation of the Chelate Effect with a Bidentate Lewis Acid," M. Biallas and D. F. Shriver, J. Am. Chem. Soc., 89, 1078 (1967).

"The Shift of Ligand Stretching Frequencies upon Coordination," D. F. Shriver and M. P. Johnson, Inorg. Chem., 6, 1265 (1967).

INVITED TALKS

"Interaction of Metal Complexes with Lewis Acids," University of Iowa, October, 1967.

"Interaction of Lewis Acids with Metal Complexes," IX International Conference on the Chemistry ofCoordination Compounds, St. Moritz, Switzerland, September, 1966.

POST TRANSITION METAL HYDRIDES

D. F. Shriver
Associate Professor, Department of Chemistry

J. A. Dilts
Ph.D. Thesis Research

This research is supported by the Petroleum Research Fund

Objective

The preparation and characterization of Cu and Zn group hydride complexes.

Approach

Cryoscopic titrations, elemental analyses, vibrational and nuclear magnetic resonance spectroscopy.

Progress

CuH is a monomer in pyridine and forms pyridine soluble phosphine complexes which are difficult if not impossible to isolate as pure solids. The complex $((C_6H_5)_3P)_2Cu\ B_3H_8$ has been prepared as a stable solid.

PUBLICATIONS

"Complexes of Trichlorostannate(II) with Ib Metals," J. A. Dilts and M. P. Johnson, Inorg. Chem., 5, 2079 (1966).

HIGHLY ENERGETIC SYSTEMS: CARBON AND HYDROGEN AT HIGH TEMPERATURE

F. E. Stafford
Associate Professor, Department of Chemistry

S. S. Lin
Postdoctoral Research Associate

G. A. Pressley, Jr.
Technical Assistant

S. J. Steck
Ph.D. Thesis Research

This research is supported by the U. S. Atomic Energy Commission.

Objective

To identify the species in equilibrium with graphite and hydrogen at temperatures of about 2000°C, and to calculate, where possible, their thermodynamic properties.

Approach

Hydrogen is passed through a reactor held at the temperature of interest. Material effusing from the reactor is collimated into a molecular beam. The molecular beam is intersected by an electron beam. Ions are formed and analyzed with a mass spectrometer. The neutral species originally present are deduced.

Progress

Equipment has been built. A series of runs (40 consecutive hours each) shows that ions with m/e up to, and probably well beyond 140 are present at 2000°C and are not due to ion-molecule reactions. The neutral progenitors of the ions are non-aromatic, highly unsaturated hydrocarbons. This is the first observation of this extensive high temperature, high molecular weight hydrocarbon system.

STUDIES OF HIGH TEMPERATURE MATERIALS: BORON HYDRIDES

F. E. Stafford
Associate Professor, Department of Chemistry

R. E. Hollins
Ph.D. Thesis Research

Objective

To identify and characterize boron hydrides that are important intermediates in boron hydride polymerization and that might be important at high temperatures.

Approach

Tetraborane carbonyl, B_4H_8CO and/or related molecules are pyrolyzed in a low pressure flow reactor. The products are analyzed directly with the high temperature mass spectrometer.

Progress

A report, giving definite evidence for the unusual species B_4H_8, was presented at the September, 1966, National Meeting of the American Chemical Society. Since that time, a vacuum line has been under construction for the synthesis and purification of the sample materials needed.

PUBLICATIONS

"Mass Spectrometric Study of Nickel Carbonyl and Its Pyrolysis," S. M. Schildcrout and F. E. Stafford, J. Am. Chem. Soc., 89, 1617 (1967).

"Electron Impact Ionization Potentials of Methyl Substituted Borazines," P. M. Kuznesof, F. E. Stafford and D. F. Shriver, J. Phys. Chem., 71, 1939 (1967).

INVITED TALKS

"Mass Spectrometric Studies of Boron Hydrides," University of Indiana, January (1967).

STUDIES OF HIGH TEMPERATURE MATERIALS: MOLYBDENUM AND TUNGSTEN OXOHALIDES

F. E. Stafford
Associate Professor, Department of Chemistry

B. G. Ward
Postdoctoral Research Associate

Objective

To identify and characterize species important in the corrosion and vapor phase mass transport of molybdenum and tungsten. The species in question are tetrahedral or five coordinated and comprise a relatively unstudied area of chemistry.

Approach

Infrared spectra are measured. Apparatus for measurement of far IR and of visible -UV spectra is under construction.

Progress

MoO_2F_2, $MoOF_4$, WOF_4, WO_2Cl_2, and $WOCl_4$ have been identified and the spectra in the region 4000 to 400 cm^{-1} have been measured.

INVITED TALKS

"Spectra and Structure of Some Gaseous Oxides, Hydroxides, and Oxohalides," Inorganic Materials Research Division Seminar, Lawrence Radiation Laboratory, Berkeley, September 25, 1967.

"Spectra of High Temperature Species," University of Michigan, March 1, 1967.

HIGHLY ENERGETIC SYSTEMS: ELECTRON IMPACT IONIZATION CROSS SECTIONS OF ATOMS

F. E. Stafford
Associate Professor, Department of Chemistry

S. S. Lin
Postdoctoral Research Associate

G. A. Pressley, Jr.
Technical Assistant

This research is supported by the U. S. Atomic Energy Commission.

Objective

To obtain cross sections for ionization by electrons with energies in the mass spectrometric range (5 to 100 ev). To develop and test various correlations, particularly for the transition element atoms.

Approach

Theoretical calculations are made using the method of Gryzinski. Experimentally, cross sections of one atom relative to another are measured using a high temperature mass spectrometer.

Progress

Theoretically, the method of Gryzinski has been used to calculate cross sections for all the atoms. Experimentally, cross sections for Ge, Sn, and Pb have been measured relative to silver. Critical comparisons have been made of the Gryzinski results with calculations of J. B. Mann, and of both of these with experiment.

MASS SPECTROMETRIC DETERMINATION OF THE IONIZATION POTENTIALS OF SELECTED TRANSITION METAL COMPLEXES

F. E. Stafford
Associate Professor, Department of Chemistry

R. G. Pearson
Professor, Department of Chemistry

S. M. Schildcrout
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

Koopman's Theorem states that, according to Molecular Orbital (MO) Theory, the ionization potential of a species is given by the energy of the highest filled orbital. It is widely used in theoretical organic and inorganic chemistry.

The purpose of the present work is to examine whether Koopman's Theorem is valid for a series of transition metal complexes and, if so, to provide an absolute calibration of MO calculations.

Approach

Since the compounds in question are relatively involatile, and sometimes thermally unstable, it was not possible to use the conventional photoionization or mass spectrometric techniques.

Because it affords high sensitivity with Knudsen introduction of samples, the High Temperature Mass Spectrometer facility was used. Using established procedures, the minimum ionizing electron energy necessary to form the parent ion is taken to be the ionization potential.

Progress

A dozen compounds have been studied and provide a clear cut example of the non-validity of Koopman's Theorem. Reasons for this breakdown are examined. The experimental work is completed and a paper is being prepared for submission.

V

MASS SPECTROMETRIC INVESTIGATION OF REACTIVE SPECIES: II GERMANES AND SILANES

F. E. Stafford
Associate Professor, Department of Chemistry

D. L. Singleton
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To identify and characterize hydrides of silicon and germanium in unusual bonding states, including those that might be of interest in high temperature systems.

Approach

Various stable compounds will be pyrolyzed at very low pressure. The reaction products will be sampled, via a molecular beam, by a mass spectrometer. If possible, the intermediates will be identified by means of mass spectra, appearance potentials, and the law of mass action.

Progress

A vacuum line is being build to synthesize the materials to be pyrolyzed.

SPECTRA OF HIGH TEMPERATURE SPECIES: RHENIUM HEPTOXIDE, PERRHENATES, OXALIC ACID, SULFUR COMPOUNDS

F. E. Stafford
Associate Professor, Department of Chemistry

M. Spoliti
Postdoctoral Research Associate

B. Pava
Undergraduate Research Assistant

This work is supported by the U. S. Army Research Office, Durham.

Objective

To obtain structural information, and from it, thermodynamic properties of model systems and of high temperature species responsible for corrosion and mass transport of refractories.

Approach

Infrared spectra are measured at temperatures up to 1600°C of the vapor species in question.

Progress

Papers on the systems $X\text{-}SO_2\text{-}Y$ (X, Y = F, OH, Cl, ..CH_3), X_2POOH, and MoO_2X_2 have been published (see below). Work on Re_2O_7, give IR spectra very similar to those of the oxohalides. The ternary oxides have spectra best approximated by a structure written $M^+ReO_4^-$.

PUBLICATIONS

"Infrared Spectra of Gaseous and Liquid-Methane-, Fluoro-, and Chloro-sulfonic Acids," S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc., 88, 4815 (1966).

"Infrared Spectra of Some Gaseous Molybdenum Oxides and Oxyhalides," T. V. Iorns and F. E. Stafford, J. Am. Chem. Soc., 88, 4819 (1966).

"Infrared Spectra of Gaseous Difluorophosphoric Acid," S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc., 88 (1966).

"Infrared Spectra and Bonding in Some $X\text{-}SO_2\text{-}Y$ Gaseous Molecules," M. Spoliti, S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc., 89, 1092 (1967).

INVITED TALKS

"Spectra and Structure of Some Gaseous Oxides, Hydroxides, and Oxohalides," Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California, September (1967).

"Spectra of High Temperature Species," University of Michigan, March (1967).

CRYSTALLOGRAPHY OF THE $\alpha \rightarrow \beta$ PHASE TRANSFORMATION OF TIN

J. T. Waber
Professor, Department of Materials Science

A. W. Ewald
Professor, Department of Physics

D. Pease
Ph.D. Thesis Research

Objective

To determine if the α - β phase transformation in tin is martensitic, that is, to prove whether it does or does not depend on diffusion as in many nucleation-and-growth phase transformations.

To determine the crystallographic relations of the transformation reaction if the shear type of diffusionless shear reaction occurs.

Approach

Basically, it is to study the reaction by means of a low temperature stage (0°C) in the electron microscope.

Initial efforts will involve preparing thin single crystal specimens of alpha tin (diamond-like structure) by Ewald's method. Next they should be free of inclusions of mercury. A technique for thinning tin to make suitable specimens for the electron microscope has been reported. This will be adapted to the present specimens. It will be possible to initiate the reaction by warming the specimen locally with the electron beam, while preventing rapid transformation of the bulk of the specimen on the cold-stage of the microscope. It will be possible to establish the relative orientation of matrix and the product phase by selected area diffraction.

Progress

No experimental work has been done to date. A considerable literature background has been developed.

PITTING OF METALS

J. T. Waber
Professor, Department of Materials Science

Objective

To determine factors contributing to the growth of corrosion pits in metals.

Approach

A large thin sheet metal sample of titanium or stainless steel held between glass walls with corrodent flowing past parallel to the free edge of the sheet. Suspicious areas of metallographically polished specimens could be examined with a travelling microscope and would be watched for the onset of pitting. Polarization characteristics of various areas could be determined.

The ultimate goal is to determine the concentration gradients and mass transfer within the growing pit, to establish better the electrochemical mechanism.

Progress

Only a portion of the contemplated equipment has been ordered to date. A potentiostat following the design of a recent British paper is being planned.

THERMODYNAMICS OF SOLID, COMPOUND SEMICONDUCTORS

J. B. Wagner, Jr.
Professor, Departments of Materials Science and Engineering Science

P. Hembree
Ph.D. Thesis Research (Completed)

JB Price
Ph.D. Thesis Research

Objective

The objective is to determine the number and type of point defects in some compound semiconductors, especially in oxides, and to relate these data to mass transport.

Approach

The plan of research is to determine the dependence of the weight change and also the electronic conductivity of partially polar semiconductors as a function of deviations from stoichiometry, doping additions and temperature. From the gravimetric measurements, the number of point defects may be inferred. From the electronic conductivity data, the type of point defects may be inferred. The chemical diffusion coefficient may also be obtained and under special conditions the self diffusion coefficient of the more mobile species may be evaluated as a function of stoichiometry. Factors which decelerate the work include the lack of good chemical analyses for the crystals used.

Progress

(1) The thermodynamics of the wustite phase field has been redetermined using a thermogravimetric technique. Results are in good agreement with the data of Darken and Gurry where comparisons are possible.

(2) The diffusion of iron in wustite at 1100°C as a function of composition has been determined. The tracer diffusion coefficient is directly proportional to the cation vacancy concentration.

(3) Tracer diffusion and chemical diffusion are being studied in single crystals of MnO.

INVITED TALKS

"The Role of Lattice Defects in Process Metallurgy," Industry Day at the Technological Institute, Northwestern University, November (1966).

"Chemical Diffusion Coefficients in Some Transition Metal Oxides," Advanced Materials Research and Development Laboratory, Pratt and Whitney Aircraft Company, North Haven, Connecticut, May (1967).

"Linear Oxidation Kinetics in High Temperature Oxidation of Metals," National Association of Corrosion Engineers, Liberty Bell Corrosion Conference, Philadelphia, Pennsylvania, September (1967).

DIFFUSION STUDIES IN PbSe AND PbTe

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Y. Ban
Ph.D. Thesis Research

T. George
Ph.D. Thesis Research (NASA Trainee)

This research is supported by the U. S. Army Office of Research-Durham.

Objective

The objective is to study mass transport in PbSe and PbTe as a function of deviations from stoichiometry.

Approach

Tracer diffusion studies have been made for the following: Se-75 into single crystals of PbS, PbSe and PbTe and Ni-63 and Pb-210 into single crystals of PbTe.

Progress

The diffusion of Se-75 in single crystals of PbS and PbSe has been carried out from 300 to 850°C. Selenium diffuses slightly more rapidly than does sulfur in crystals of PbS annealed under argon. When a comparison is made at the same temperature, selenium diffuses more rapidly in PbSe than in PbS.

The diffusion of Ni-63 into PbTe yields a penetration profile which exhibits "anomalous behavior". A p-n junction migrates into the crystal with time.

STUDIES CONTRIBUTING TO AN UNDERSTANDING OF REDUCTION OF OXIDES

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W. J. Hillegas
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L. Laub
Ph.D. Thesis Research

This research is supported by the American Iron and Steel Institute.

Objective

The objective is to study the defect structure of iron oxides and to correlate this with mass transport in these oxides.

Approach

The d.c. electronic conductivity and the Seebeck coefficient of wustite and wustite doped with mono-, or tri- or tetra-valent impurities are being studied.

Progress

Measurements of the Seebeck coefficient as a function of grain size and also as a function of magnesium doping show that:

(1) The p to n transition in wustite is not due to the presence of grain boundaries since the Seebeck coefficient is found to be independent of grain size.

(2) Doping wustite with magnesium enlarges the p-type region of the phase field.

INVITED TALKS

"Research on the Defect Structure of Wustite," Research Laboratory of Inland Steel Company and Calumet Campus of Purdue University, East Chicago, Indiana, May (1967).

ELECTRONIC TRANSPORT STUDIES ON PbS AND PbSe

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P. L. Anderson
Ph.D. Thesis Research

W. Johnson
Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

The principal technical objective is to study the carrier concentrations in single crystals as a function of deviations from stoichiometry and doping additions. These data are to be correlated with diffusion measurements performed on similarly prepared crystals.

Approach

Four point conductivity, Hall effect and Seebeck measurements are made at room temperature on carefully prepared single crystals. In addition, Seebeck measurements over the temperature range 77-500°K, Hall effect and magnetoresistance measurements over the range 4-400°K are being made in an effort to characterize completely the electronic structure of the materials.

Progress

The problem of retrograde solubility in these lead salts is being studied as a function of the pre-equilibration treatment and quench rates. The homogeneity of these samples is investigated with a room temperature Seebeck test. Initial studies of room temperature Seebeck versus carrier concentration for PbS are comparable to the recent data of A. J. Strauss (Trans. AIME, 1967). Although data for the lead-lead sulfide phase boundary at higher temperatures is in good agreement with that of Strauss, the lower temperature data indicate a single phase region that is narrower. Samples of PbSe prepared by the conventional dew-point equilibration technique are not homogeneous by the Seebeck test. This remained true for samples equilibrated up to 60 hours under conditions in which equilibrium should have been attained in one hour. Current efforts are trying to relate the measured quench rates with homogeneity.

INVITED TALKS

"The Defect Structure of Lead Sulfide,"

(a) University of California, Berkeley, February (1967).

(b) University of Utah, Salt Lake City, February (1967).

DISLOCATION THEORY

J. Weertman
Professor, Department of Materials Science

Objective

To develop further the theory of dislocations in crystals as applied to deformation of solids.

Approach

With the use of dislocation theory of a linear elastic solid.

Progress

(1) A theory of supersonic and transonic dislocations has been developed. From this investigation it is concluded that a dislocation that runs on a plane that gives up energy and whose force law does not change sign must run at a supersonic speed. If energy is given up but the force law changes sign the dislocation runs at a transonic speed. An ordinary dislocation pushed by an applied stress has a limiting velocity that lies in the transonic velocity range and not at the slow sound velocity as is usually assumed in the literature.

(2) The stress and displacement field of a climbing dislocation has been determined. It is shown that climbing dislocations of like sign attract each other when their velocities are greater than the Rayleigh wave velocity.

(3) A direct calculation has been made of the energy required to cause coalescence of dislocations. It is shown that this energy is always positive for two dislocations of like sign even if the forces between the dislocations are attractive.

PUBLICATIONS

"Coalescence Energy of Two Moving Dislocations of Like Sign," J. Weertman, J. Appl. Phys., 37, 4925 (1966).

"Stress and Displacement Fields of an Edge Dislocation that Climbs with a Uniform Velocity," J. Weertman, J. Appl. Phys., 38, 2612 (1967).

INVITED TALKS

"Supersonic and Transonic Dislocations," U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, August, 1967.

"Conditions at the Bottom of Ice Sheets," Glaciology Society, Hanover, New Hampshire, October, 1966.

"Conditions at the Bottom of Ice Sheets," University of Western Ontario, Canada, October, 1966.

HIGH PRESSURE

J. Weertman
Professor, Department of Materials Science

Objective

To determine the equation of state of minerals and rocks which could be present in the upper mantle. Application would be to relate this elastic constant to the measured seismic velocities in order to learn something about temperature and composition in the upper 300 Km of the earth.

Approach

A high temperature piston cylinder device is used to achieve the conditions of 450°C and 40 Kb. A solid pressure medium such as lead or gold is used. The data are all related to the 30°C compressibility of iron.

Progress

This project has been completed and is described in the Ph.D. Thesis of Dr. P. N. LaMori.

HIGH VELOCITY DISLOCATIONS

J. Weertman
Professor, Department of Materials Science

V. R. Parameswaran
Ph.D. Thesis Research

Objective

To study and obtain dislocation velocities close to the transverse sound velocity.

Approach

Short stress pulses are applied to a sample and dislocation motion is measured using the etch-pit technique.

Progress

In the study of dislocation motion in zinc, basal dislocation velocities up to about 6×10^4 cm/sec were observed which corresponds to 0.26 times the shear sound velocity in the material.

PUBLICATIONS

"Theory of Infinitesimal Dislocations Distributed on a Plane Applied to Discontinuous Yield Phenomena," J. Weertman, Canadian J. Phys., 45, 797 (1967).

"The Jog-Dragging Screw Dislocation Model for Steady-State Creep," J. Weertman, Acta Met., 15, 1081 (1967).

INVITED TALKS

"Dislocation Climb Versus Jog Dragging Screw as the High Temperature Creep Mechanism," Massachusetts Institute of Technology, March, 1967.

"Dislocation Climb Versus Jog Dragging Screw as the High Temperature Creep Mechanism," Brown University, March, 1967.

"Discontinuous Yielding," Rice University, March, 1967.

"Fatigue of Metals and Dislocation Theory," AGARD Meeting, Turin, Italy, April, 1967.

"Theory of Dislocation Distribution on a Plane Applied to Discontinuous Yielding," Los Alamos Laboratory, January, 1967.

"Theory of Dislocation Distribution on a Plane Applied to Discontinuous Yielding," Cornell University, February, 1967.

Discussion Chairman. High Speed Dislocation, Battelle Conference on Dislocation Dynamics, Seattle, Washington and Harrison Hot Springs, B.C., May 1967.

FATIGUE OF METALS

J. Weertman
Professor, Department of Materials Science

H. Ishii
Ph.D. Thesis Research

A. Purcell
Ph.D. Thesis Research

This research is supported by the Office of Naval Research.

Objective

To investigate factors influencing the rate of growth of fatigue cracks, such as cyclic stress, static mean stress, plastic zone, microstructure, environment, and so on.

Approach

Sheet specimen with initial slit in the center is subjected to cyclic stressing. By telescope, macroscopic growth rate can be measured anytime without stopping the test. Also information on growth rate can be obtained from microfractography by measuring the distance between striations. To study the environment effect a vacuum chamber with viewing window will be used.

Progress

(1) A series of crack growth measurements have been conducted on pure aluminum and 2024-T3 aluminum alloy specimens. It was found results agreed reasonably well with the equation derived from the theory of infinitesimal dislocations by Weertman.

(2) By using replica technique, study on fractured surface has been done. Not enough data are yet available to discuss this quantitatively.

THERMODYNAMICS OF ALLOYS

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D. Bartosik
Ph.D. Thesis Research

R. Jones
Ph.D. Thesis Research

P. K. Raychaudhuri
Ph.D. Thesis Research

F. E. Stafford
Associate Professor, Department of Chemistry

Objective

The primary goal is to elucidate those factors which contribute to the equilibrium state of binary metallic solid solutions. Particular emphasis is placed on evaluating the extent to which various factors contribute to the observed excess thermodynamic functions of the alloy systems studied.

Approach

Elevated temperature thermodynamic quantities for solid solutions are determined by: (1) employing a heated, two-chamber Knudsen effusion cell and a mass spectrometric detection instrument for activity measurements; and (2) utilizing a liquid tin solution calorimeter for measurements of the internal heats of mixing. The vibrational excess entropy for solid solutions is being evaluated by determining the Debye characteristic temperature from integrated intensities of an x-ray diffraction spectrum obtained at an elevated temperature.

Progress

Activity measurements on a complete series of Au-Pt alloys have been accomplished over the temperature range 1100-1300°C with the aid of the two-chamber Knudsen effusion cell technique. These data indicate a substantial positive departure from Raoultian behavior at all compositions and temperatures investigated. The partial heats of mixing for gold appear to be negative for alloys containing more than 80 at.% Au, and positive otherwise. X-ray measurements of Debye temperatures are continuing but with limited success. Construction of the liquid tin solution calorimeter has been completed, but testing of it is still in progress. The initial calorimetric measurements will be done on Au-Pd alloys thermally equilibrated at elevated temperatures prior to dropping into the tin bath. To resolve a controversy existing among earlier published results, our next activity experiments will be undertaken on Ag-Pd solid solutions and these will be followed by similar observations on Au-Pd alloys.

MASS TRANSPORT IN IONIC CRYSTALS

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Ph.D. Thesis Research

C. Bauer
M.S. Thesis Research

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Undergraduate Co-Op Student

This research is supported by the U. S. Air Force Aerospace Research Laboratory, the Office of Naval Research and the Advanced Research Projects Agency

Objective

To investigate the dominant lattice disorder of ionic solids and to relate the defect structure to observed tracer diffusion coefficients obtained on pure and doped crystals of these materials.

Approach

The dominant lattice disorder of ionic compounds is investigated by measuring the ionic conductivity of crystals containing known concentrations of aliovalent cations isothermally. Such dopants change the concentration of lattice defects, preserve charge neutrality and chemical equilibrium, thereby allowing accurate values of the heats of formation and defect concentrations to be obtained. Ionic transference numbers are measured by Tubandt and blocking-electrode experiments. Two-isotope tracer diffusion experiments on undoped crystals, conducted in the presence of an externally applied dc field, are used to determine the correlation factor, the diffusion coefficient and ionic mobility of the tracer.

Progress

The ionic conductivity experiments are just beginning and will likely focus on NaF, both pure and doped; the ionic conductivity results of Lehfeldt and the transference number results of Tubandt on pure NaF will be confirmed first. These conductivity observations will then be extended to crystals doped with known amounts of a divalent ion, probably Cd^{2+} or Mn^{2+}. A Chelma diffusion and drift mobility experiment will be undertaken using Na^{24} and Na^{22} tracers; and the drift of the tracer concentration profile and charges of its shape under diffusion will be followed. Such observations should yield values of the tracer drift mobility as well as its diffusion coefficient.

DIELECTRIC AND ANELASTIC RELAXATIONS IN IONIC COMPOUNDS

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G. Fehr
Ph.D. Thesis Research

This research is supported by the U. S. Air Force Aerospace Research Laboratory and the Office of Naval Research.

Objective

Measurements of dielectric and anelastic relaxation effects in ionic crystals containing point defects are being made to identify the defect complex responsible for the relaxation and to describe its local symmetry.

Approach

The linear, reversible, time-dependent response of an ionic crystal containing point defects to alternating electrical or mechanical stress fields is followed by measuring dielectric and anelastic loss as a function of temperature and frequency. The origin of such relaxations stems from the redistribution of the defects among sites which are initially equivalent but which become inequivalent in the presence of the external field. The measured ratio of mechanical-to-electrical relaxation times is compared with theoretical predictions from many-position models to determine the local symmetry of the atomic arrangement about the point defect.

Progress

Observations of dielectric relaxation in specimens of Dy-doped CaF_2 have continued. While relaxation peaks are apparent in plots of log tan δ vs T^{-1}, good separation of the peak from the background was obtained only in the case of specimens doped with 0.15 and 0.25 mole % DyF_3. These data could be represented by a single relaxation time Debye peak. Work on doped CaF_2 is continuing and new experiments are being undertaken on both Tb_7O_{12} and NaF, doped with various aliovalent cations. Construction of a Förster-type internal friction apparatus has been completed to aid in the observation of mechanical relaxations in these systems.

DRIFT MOBILITIES OF CHARGE CARRIERS AND SPACE-CHARGE-LIMITED CURRENTS IN LOW MOBILITY SEMICONDUCTING MATERIALS

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Postdoctoral Research Associate

This research is sponsored by the Office of Naval Research and U. S. Air Force Aerospace Research Laboratory.

Objective

The investigation of carrier drift mobilities and carrier trapping in high-resistivity, photoconductive semiconducting materials exemplified in Li-doped ZnO and selected glasses.

Approach

Measurements of carrier drift mobilities in semiconducting materials as a function of temperature are accomplished by determining the time of transit of electrons across a specimen which had been photoinjected at one surface by light pulses of 10^{-8} second duration. Such measurements permit detailed investigation of shallow electron traps (arising from imperfections) which are able to establish equilibrium with injected electrons in the conduction band in times less than the carrier transit time across the specimen. The use of ohmic metal electrodes allows the injection of electrons into thin, plane-parallel crystals of oxides and glasses which produce space-charge-limited currents at high fields. These latter experiments are useful in the investigation of electron trapping levels in the vicinity of the steady-state Fermi level.

Progress

The measurements of electron drift mobilities and lifetimes and space-charge-limited currents in Li-doped ZnO monocrystals have been completed for two crystallographic orientations over the temperature range 250 to 400°K. These observations indicated: (1) electron traps of density 10^{16} cm^3 are located 0.29 eV below bottom edge of conduction band; (2) electron lifetimes at 300°K ranging from 30 - 100 x 10^{-6} sec; (3) discrete or narrow bands of trap levels exist at 0.4 and 0.72 - 0.8 eV below conduction band edge. The drift mobility and space-charge-limited current measurements are continuing on ZnO doped with either trivalent or other monovalent cations and on As-Se-Te photoconductive glasses.