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Semi-Annual Status Report #16
on
NASA Research Grant NsG-6-59
Covering
Research on the Physics of Solid Materials
For the Period
1 November 1966 through 30 April 1967

Under the Direction
of
Franz R. Brotzen
H. E. Rorschach, Jr.
and
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I. Introduction

Research in the areas of Materials Science and Solid State Physics and Chemistry at Rice University has been supported principally during the past eight years by National Aeronautics and Space Administration Grant NaG-6-59. The goals of this grant have been the following:

1.) To promote the growth of significant research in solid materials. Work relevant to the goals of NASA in the field of solid materials is being given priority.

2.) To increase the competence of graduate students and staff in the area of solid materials.

3.) To broaden the competence of workers in solids by encouraging interdisciplinary cooperation at all levels.

To achieve these goals, funds from this grant have been used to support research in areas involving workers from six University departments. As a consequence of this support, during the past six months, the accomplishments listed below were made possible.

1.) The program involved 17 faculty members, 32 graduate students, and 7 post-doctoral fellows. Significant research results bearing on basic problems in solid materials have been obtained. These results are described in Section II.

2.) A new seminar program for faculty and graduate students interested in solid materials has been organized for the discussion of current research problems. The first year program (described below) was comparatively successful, but improvements are planned.

3.) Interdisciplinary cooperation is still increasing as a result of the day-to-day contact made possible by the occupancy of the new Space Science building by workers in Materials Science from several departments.

The Research Report given in Section II has a new format that was initiated with our last progress report. We have again divided the research work on solids into five major areas, and a status report
for each area has been prepared by a staff member in that area. The authors are different than those of the previous progress report. As a consequence, some work that was treated in detail in the previous report is here mentioned only briefly; other work is treated more fully in this report. Over a period of time, one can expect to find reports in considerable detail on almost every piece of research. These reports are intended to be less technical and more descriptive than in the past. An attempt has been made to place the work at Rice in perspective with respect to the whole field of solids as well as provide a report of recent progress. We are still some distance from real success, but efforts will be continued to improve these reports so that they may be of wider interest and use to those who receive them.

During the past six months a successful interdisciplinary working seminar program was completed. Meetings were held weekly and were attended by faculty and graduate students from electrical engineering, materials science and physics. The speakers were either faculty members or advanced graduate students who discussed research topics of current interest to them. Recent topics were:

1.) Magnetic Properties of Rare-Earth Elements
2.) Coherency and Solid State Lasers
3.) A Dislocation Model of Continuous Yielding
4.) Flux Motion in Superconductors
5.) Short Range Order in Alloys
6.) Helium 3-Helium 4 Dilution Refrigerators
7.) Direct Observation of Atoms in Metals by Field Ion Emission Microscopy
8.) Micro-Chemical Analysis by Cyclotron Bombardment
This program was well attended and often produced a lively exchange of views. It will be continued (and improved) next year.

A list of publications accepted and published during the period of this report is given in Appendix I.
II. Research Report

The research work on solids of 25 different projects supported by this grant divides naturally into five areas:

1.) Defect Structure and Mechanical Properties
2.) Electrical and Optical Properties
3.) Magnetism and Superconductivity
4.) Thermodynamics and Solid Surfaces
5.) Thin Film Properties

A report has been prepared in each of these fields by one of the research staff in that field. These reports are given below, together with a listing of the staff working in each field. The reports are intended to present some perspective on the field in question, as well as enumerate recent research accomplishments. Further details of some of this work may be found in the publications listed in Appendix I.

A. Defect Structure and Mechanical Properties--J. M. Roberts

Staff: F. R. Brotzen, Professor of Materials Science

J. M. Roberts, Associate Professor of Materials Science

M. L. Rudee, Assistant Professor of Materials Science

In the preceding report of this series (Semi-Annual Status Report #15) a general description was presented of five types of studies in the field of defect structure and mechanical properties which are active at Rice University. These were:

1.) Plastic Deformation of Body-Centered Cubic Crystals

2.) Experimental Verification of the Relation Between Short-Range Order (SRO) in Alloys and Their Electrical Resistivity

3.) Microstrain, Microcreep, and Amplitude Dependent Dislocation Damping in Metal Crystals
4.) Ultrasonic Attenuation in LiF, Nb and Ta Crystals in the Megacycle Frequency Range from 2°K to 300°K

5.) Stage I Deformation in Hexagonal Close-Packed Crystals.

Since no new studies have been initiated in this area in the past months, a similar format will be used to describe the recent progress. The present description should be considered as a supplement to the more general review presented in the previous status report.

1.) Plastic Deformation of Body-Centered Cubic Metals

The overall objective of this research is to gain an understanding of the fundamental mechanisms of plastic flow of BCC transition metals and apply the knowledge gained to the interpretation of the mechanical behavior of this important group of materials.

During the past few years a great deal of experimental research into the mechanical behavior of molybdenum crystals was undertaken under the sponsorship of this grant. The principal investigator, Dr. F. R. Brotzen was on sabbatical leave from the Rice University for the academic year 1966/67 and devoted much of his time to establish a model that would lend itself to quantitative treatment and that could interpret the wealth of experimental results.

The observed phenomena stated in earlier Status Reports, which any proposed model must account for in a satisfactory manner, include notably:

a.) The great rise of the flow stress in the body-centered cubic metals at low temperatures or at high strain rates.

b.) The relative immobility of screw dislocations at low temperatures, which changes to moderate mobility above a
critical temperature.
c.) The unusually low activation volume at low temperatures in these metals, as compared to that of close-packed metals.
d.) The rather sudden rise of the activation volume above a critical temperature which corresponds roughly to that in (b).
e.) The copious generation of point defects during plastic flow at low temperatures, which tends to decrease as the above critical temperature is exceeded.
f.) The unusual transition-creep curves of these metals, which are characterized by very high strain rates which decay rapidly after a small incremental stress is applied.

The model presently under investigation considers a separate treatment of screw-dislocation and edge-dislocation elements. While edge dislocations are thermally activated in overcoming small Peierls-Nabarro potentials and pinning points produced by foreign atoms, screw dislocations are held up primarily by jogs. At low temperatures, screw dislocations move primarily by the creation of point defects, a process that does not involve thermal activation. Additional motion of screw dislocations particularly at moderately low temperatures, may take place as a result of conservative movement of jogs and subsequent annihilation. Since screw dislocations are thought to be extended, the conservative motion of jogs is a thermally activated process. Only after conservative jog motion becomes substantial in relation to the velocity of a screw dislocation, will the generation of point defects at jogs turn into a thermally activated process characterized by a high activation volume. Preliminary analysis shows promising
results, although a great deal of further calculation will be required.

To investigate variations in the width of screw dislocations, an experimental program is presently under way. This program aims at varying the stacking-fault energy through the introduction of rhenium into the molybdenum. The preliminary phase of this experimental project consists of the determination of elastic constants of the molybdenum-rhenium alloy crystals.

The future plans for this work are the continuation of the experimental program, which is expected to yield interesting results within the next year, and further computations based on the aforementioned model.

2.) Experimental Verification of the Relation Between Short-Range Order (SRO) in Alloys and Their Electrical Resistivity.

Although SRO (clustering) is nearly a universal property of solid solutions, few accurate measurements of SRO have actually been accomplished. This is due, in large part, to the laborious nature of diffuse x-ray peak measurements. Two improvements have been developed that greatly facilitate the measurement of SRO. A theoretical analysis has been performed to minimize the number of points in reciprocal space that need be measured. In addition, some geometrical corrections have been developed that improve the accuracy of the data.

These techniques have been tested on a single crystal of Cu₃Au. Only four hours were necessary to collect data, compared to the several weeks previously required. In SRO measurements there is a built-in test of the accuracy of the data; the true
value of the zero order SRO coefficient is necessarily unity. Using the present method, a value of 1.04 was obtained, the closest agreement to theory yet reported.

3.) Microstrain, Microcreep and Amplitude Dependent Dislocation Damping in Metal Crystals.

The objectives of this research are:

a.) to complete the initial phases of calculating the amplitude dependent internal friction due to dislocation-dislocation interactions with application to damping data and

b.) to continue an experimental study of stress relaxation in molybdenum, tantalum, niobium, and tantalum-rhenium single crystals in conjunction with theoretical analysis of stress relaxation phenomena.

A computer analysis of the breakdown of attractive dislocation junctions, a mechanism contributing to anelastic hysteresis, has been completed. A Gaussian distribution function was assumed for the dislocation loop lengths and equations predicting the bowing strain, modulus defect, energy loss, and decrement as a function of stress, distribution width and dislocation density have been developed. Normalized curves have also been developed for the energy loss and decrement due to this mechanism as a function of the reduced shear stress (the applied shear stress divided by the shear modulus of the crystal). The predictions are in fair agreement with low frequency high amplitude internal friction data for copper single crystals obtained in our laboratory. Other distribution functions such
as the Koehler distribution have been investigated, but the Gaussian seems to produce the best agreement with the copper data.

The analysis of damping in magnesium single crystals due to dislocation-dislocation intersections at repulsive-type junctions is now complete. Internal consistency between experiment and analysis has been obtained based upon this single mechanism, even though a distribution of activation energies and volumes are associated with it. This work will be presented and published as part of the Proceedings of the International Conference on the Strength of Metals and Alloys, Tokyo, September, 1967.

The stress relaxation study of molybdenum single crystals has been completed and the data are being analyzed. These experiments were performed on randomly oriented single crystals in the prestrain range of 0.005 to 0.05 and for a temperature range of 77 to 442°C. The results can be explained by a theoretical model that is a simple extension of the stress relaxation theory at constant total strain. The principal observations are:

1.) the activation volume increases with temperature and decreases with prestrain or stress at constant temperatures.
2.) the activation enthalphy increases with temperature at constant prestrain.
3.) the data suggest that two mechanisms or processes are
operative in the temperature range investigated. The transition temperature is near 230°K.

This work is now ready for preparation of a manuscript for publication.

The future plans for this work are to carry out a general analytical treatment of stress-relaxation theory. The stress dependencies of the attack frequency, activation length, activation distance, and activation entropy are presently being examined for rigid and non-rigid barriers.

4.) Ultrasonic Attenuation of LiF Crystals Between 2°K and 300°K (under the supervision of Dr. J. M. Roberts).

The objectives of this research are:

a.) to study in detail the overdamped dislocation resonance peak in LiF crystals between 77°K and 300°K,

b.) to investigate electron damping of dislocations in prestrained niobium and tantalum in the normal and superconducting states,

c.) to investigate the effect of stress bias upon the decrement and modulus defect due to dislocations in lithium fluoride in the magacycle frequency range,

d.) to study the effect of lithium precipitates in lithium fluoride due to Co^{60} irradiations and other irradiations via magacycle range ultrasonic attenuation.

No further experiments have been performed since the last report. Calculations by this author indicate the decrement due to point defect-dislocation-fluxoid interactions in the normal, mixed and superconducting states of niobium is too small to be detected by the 1 cps internal friction torsion pendulum technique.
5.) **Stage I Deformation in Hexagonal Close-Packed Crystals.**

The experimental study of the activation volume, work hardening coefficient and flow stress of cadmium single crystals deformed in shear is now complete. It was incorrectly stated in the last report that tensile and shear specimens yielded different results. In effect, the data on shear specimens do exhibit similar anomalies as were previously observed for tensile specimen single crystals. It now seems that these effects are intrinsic to easy glide behavior in cadmium. Some investigators have seen somewhat similar effects on the work hardening coefficient in zinc, but have not made a serious effort to explain it, i.e., the work hardening coefficient goes down with decreasing temperature in the temperature range below that of extensive recovery.

A computer study is currently in progress to investigate the effect of several operative dislocation processes upon the macroscopically observed parameters: the flow stress, the work hardening coefficient, and the apparent activation volume.

**B. Electrical and Optical Properties—L. E. Davis**

**Staff:** L. E. Davis, Assistant Professor of Electrical Engineering

G. C. Jain, Associate Professor of Electrical Engineering

R. B. McLellan, Assistant Professor of Mechanical Engineering

T. A. Rabson, Associate Professor of Electrical Engineering

H. E. Rorschach, Professor of Physics

M. L. Rudee, Assistant Professor of Materials Science

G. T. Trammell, Professor of Physics

The current research at Rice considers some aspects of the behavior of matter in static electromagnetic fields and alternating fields with
frequencies up to $10^{19}$ Hz. Within this wide frequency range, the language, the conceptual approach and especially the experimental techniques are very different.

1. Static and "Low-Frequency" Properties (D. C. and frequencies below $10^8$ Hz.)

   a.) Gravitationally-Induced Electric Field in a Conductor

   An interesting problem that has been considered recently by Professors Rorschach and Trammell in collaboration with Professors Dessler and Michel of the Space Science Department is the calculation of the gravitationally-induced electric field in a conductor. With considerable over-simplification, it may be said that the effect occurs in a conductor at rest when the electrons and positive ions tend to "settle" as a result of the gravitational field. Under the influence of gravity alone the electrons and ions would assume different spatial distributions as a result of their different densities; hence a static electric field will be established. The resultant field is calculated to be of the order of $10^{-6}$ volts/meter, which is four or five orders of magnitude larger and of opposite sign to that predicted by previous workers. This work has suggested a new way to study some properties of the Fermi surface in metals.

   b.) Direct Energy Conversion

   The conversion of energy from one form to another in solid-state devices has, in principle, applications in heating and refrigeration systems and solar batteries. Professor Jain and his students are studying the efficiency
of some of these phenomena, and the electrical and thermal properties required to maximize the effects. Attention is currently being given to thermoelectric and thermomagnetic effects and photocells.

The thermoelectric effect is well known from its widespread application in metal-junction thermocouples. However, larger effects are seen in semiconductor-metal junctions and the principle may be summarized as follows: When electrons pass from the semiconductor to the metal their energy is reduced and heat is given off. Alternatively, if the current is reversed, only higher energy electrons pass from the metal to the semiconductor and heat is absorbed in order to reestablish proper thermal redistribution of the electrons in the metal. These effects are reversible.

The thermomagnetic effect may be described as follows: If a magnetic field is applied perpendicular to a thermal gradient in a semiconductor, an electric field will be produced orthogonal to both the magnetic field and the thermal gradient. Conversely, crossed electric and magnetic fields will produce a thermal gradient.

The materials presently being investigated are a Si-Ge alloy and Sn doped and Te doped Bi-Sb alloys. Measurements have shown that Sn doped Bi-Sb alloys are semiconductors below 135°K, and that this alloy may be useful for thermoelectric cooling at low temperatures. A theoretical study has also been conducted to determine the optimum carrier
concentration for a single stage and infinite stage thermoelectric generator. It has been found that, for lattice scattering the optimum carrier concentration increases with increasing hot junction temperature, while the reverse is true for ionized impurity processes. Contact resistance is important in these devices and a vacuum oven has been designed to permit measurement of the temperature dependence of this parameter.

Another form of energy conversion is that of light into electricity. When light is absorbed by a semiconducting element, equal and opposite charge carriers may be generated. If this occurs in the presence of an electric field, such as in the region of a p-n junction, the carriers are swept in opposite directions and a direct current is produced. There are several forms of losses that degrade the efficiency, three of which are optical reflection at the surface, carrier recombination, and spectrum losses. The latter arise since the lower frequency components of the incident spectrum will have too little energy to produce electron-hole pairs and higher frequencies will form pairs but the excess energy will be dissipated as heat.

A useful figure of merit for a photovoltaic cell is the "Quantum Efficiency". This is the ratio of the maximum rate at which minority carriers cross the junction to the rate at which electron-hole pairs are created by absorbed monochromatic radiation. Whereas earlier workers assumed that diffusion was the only mechanism for moving carriers
toward the junction, Professor Jain and his co-workers have analyzed a model that includes a variable drift field arising from the impurity density gradients. Their conclusions from this model are borne out in some respects by experimental results obtained elsewhere, but detailed comparison with experiment is needed, and to this end preparations have been made for the controlled fabrication and testing of graded impurity photocells.

2.) **Microwave Properties** (Frequency approximately $3 \times 10^9$ Hz. Wavelength approximately 10 cms.)

   a.) Microwave Losses in Ferroelectrics

   Ferroelectricity is the spontaneous electrical polarization that may occur in a crystal, and which can be reversed with a small applied electric field. Although the behavior is well known, prediction and analysis are difficult. It is potentially useful to be able to control electrically the polarization of a material and so control the propagation of an electro-magnetic wave through it. At microwave frequencies, however, the wave is too strongly attenuated to permit any microwave applications of the ferroelectric effect.

   Of the many ferroelectric materials, the most extensively studied is Barium Titanate ($\text{BaTiO}_3$), and the losses in this material at $3 \times 10^9$ Hz. have been measured by Professor Davis and his students. $\text{BaTiO}_3$ exhibits spontaneous polarization at temperatures below 120°C, the Curie temperature, and the losses were measured as a function of temperature in both single-crystal and ceramic specimens. The dielectric constant
at this frequency is approximately 1000 with a loss tangent of 0.45, and at the Curie temperature these values rise to 4000 and 0.55. The large losses have been attributed by some workers to the d.c. conductivity but the present work does not agree with this explanation. Previous work by Professor Jain had shown that doping BaTiO₃ ceramic with 0.04% Indium lowered the d.c. conductivity by two orders of magnitude. Calculations show, and microwave experiments confirm, that losses in this doped material are not measurably different from those in the undoped ceramic. The losses are more likely to arise from the vibrations of the Ti⁴⁺ ions in the oxygen octahedras as suggested by Cochran.

3.) Optical Properties (Frequency approximately $0.5 \times 10^{15}$ Hz. Wavelength approximately $0.6 \times 10^{-6}$ m.)

a.) Polarization and Coherence in Lasers

Until recently, coherent electromagnetic radiation could not be generated at frequencies above $0.3 \times 10^{12}$ Hz. The introduction of the optical maser about seven years ago remedied this situation, but although this device is generally stated to be a coherent source it is in fact only partially coherent. Professor Rabson and his students have measured the polarization of individual spikes within each laser pulse, and also the variation of polarization with power level and with different materials. The percentage polarization increases to approximately 100% as the power level is lowered to approach the threshold value, and the polarization tends to be related to the crystalline axes when such
axes are present. However, the polarization differs from spike to spike. Further details are available in the previous progress report. To investigate temperature broadening effects, the polarization from a Nd$^{3+}$ glass laser at 77°K has been measured, and little variation from room temperature operation was observed.

These experiments have stimulated the discussion of questions concerning definitions of terms like "polarization", "coherence" and "resonant modes." A theoretical study is about to be concluded of the basic connection between the polarization of light and the intrinsic angular momentum of light which brings out many analogies between light beams and particle beams. Associated experimental work is also being considered in order to check the theory and clarify some of these analogies.

b.) Lasers and Surface Chemistry

This group is also working with Professor Margrave of the Chemistry Department. Final preparations are being made to use a laser as a source of energy for vaporizing targets in a time of flight mass spectrometer. This should make possible the analysis of the surface of samples of almost any solid. In addition to mass spectroscopic analysis it is hoped that optical analysis may also be performed on the sample tested.

4.) X-Ray and Gamma-Ray Interactions (Frequency approximately $10^{18}$ Hz. Wavelength approximately $10^{-10}$ m.)

At the higher end of the frequency spectrum there is X- and γ-radiation, which is usually incoherent and of large spectral
However, the Mössbauer effect, which was described in the previous progress report, is a process that causes γ-ray emission with an extremely small frequency spread. A group directed by Professor Trammell has developed an optical theory of these rays, and as an application of this theory they have investigated the possibility of using very coherent Mössbauer γ-rays for lensless microscopy of molecules. However, they have shown that molecular microscopy using X-rays or neutrons, quite apart from technological details and difficulties, is in principle impossible. This is due to quantum limitations which insure the destruction of the molecule before it can be "observed" by these radiations. Electron microscopy and in some cases field emission microscopy, are, according to their findings, the only possible means for molecular microscopy in which the individual atoms are resolved.

There are many means by which the Mössbauer effect can be used to study solids. One application is the determination of the Debye frequency of $^{57}$Fe in a solid solution by use of the second-order Doppler shift. This technique has been experimentally tested, but it has not been applied in a systematic manner. The information gained by this method is unique since it seems to be the only direct method for studying the vibrational properties of an impurity atom in a metal. The second-order Doppler shift is now being used by Professors McLellan and Rudee to study the concentration dependence of the vibrational frequency of iron in platinum and palladium. Experimental apparatus for the first measurements is being assembled.
C. Magnetism and Superconductivity—P. L. Donoho

Staff: H. C. Bourne, Professor of Electrical Engineering
      P. L. Donoho, Associate Professor of Physics
      W. V. Houston, Professor of Physics
      H. E. Rorschach, Jr., Professor of Physics

In this area of research, work is being carried out on the fundamental magnetic and magnetoelastic properties of a relatively new class of magnetic materials: the lanthanide series of elements, commonly called the rare earths. In addition, research on several aspects of superconductivity is also being conducted. Since these two areas of research differ substantially in their goals and methods, they are treated separately in what follows. Other work on magnetism (the magnetic properties of thin films) is discussed in section E.

1.) Microwave Magnetic Resonance and Non-Resonant Absorption in Single Crystals of Dysprosium.

In this area Professor Donoho and his students are conducting both theoretical and experimental studies of elements in the lanthanide series, concentrating heavily at present on the element dysprosium, in single-crystal form. Dysprosium, as well as most of the elements in the latter half of the lanthanide series, exhibits strong magnetic properties quite different from those of the better-known iron-group elements. Some of the more striking properties include the existence of both ferromagnetic and antiferromagnetic phases, enormous magnetostriction, and very large values of the saturation magnetization in the ferromagnetic phase.

In dysprosium, which is now readily available in high purity single-crystal form, these properties are more pronounced
than in many of the other elements. There is also reason to believe that theoretical attempts to understand these properties will be more successful than for the other lanthanides. Consequently, dysprosium has been the object of most of the research in this area. In addition to the advancement of fundamental understanding of the magnetic properties of dysprosium, one goal of the research being conducted under this grant is the development of an ultrasonic transducer employing the enormous magnetostrictive effect which has been already observed in dysprosium. Such a transducer would be capable of operation at microwave frequency with very high efficiency, and would have important applications in many branches of science and technology. For example, the predicted efficiency of a transducer now under development would be about ten per cent at a frequency of 10,000 MHz, about a 100-fold improvement over existing transducers. Such a high efficiency would permit experiments in ultrasonics comparable to those optical experiments which only became possible with the advent of the laser.

In the course of research during the period covered by this report, Professor Donoho and his students have been primarily concerned with magnetic-resonance studies at microwave frequencies. This work has shed new light on the important part played by magnetostrictive effects on most of the magnetic properties of dysprosium. This work has also led to a new determination of the strength of some very important anisotropy effects which are closely related to the magnetostriction. For the immediate future, the research will concentrate on theoretical understanding of
2.) **Superconductivity.**

Superconductors have become technologically important because of their use in high-field magnets and in sensitive control circuits. There are prospects for their use as generators and detectors of high-frequency electromagnetic radiation and as detectors of small magnetic fields. Important for all these applications is the so-called Type II superconductor, in which the normal superconducting state is modified by the appearance of magnetic vortices when a magnetic field is applied to the superconductor. Much of the work in superconductivity being carried out at Rice under this grant is concerned with studies of magnetic interactions in various superconductors which will have a bearing on such things as the dynamics of vortex motion in superconductors.

Professor Rorschach and his students have been primarily concerned with the magnetic properties of molybdenum. There is evidence from "flux-trapping" experiments that vortices may be present in this material even though it is not a Type II superconductor. Research has been directed toward studying the nature of the trapped flux, both experimentally and theoretically, in order to understand the conditions under which the vortex structure can appear as trapped flux. Measurements have been made, using a He³ cryostat, of the magnetic properties of molybdenum over the temperature range from 0.9°K (the superconducting transition temperature) down to 0.4°K. The dynamics and reversibility of the Meissner effect (the exclusion of magnetic flux from a
superconductor) have been studied thoroughly, as has the so-called supercooling field, whose value permits an accurate determination of the surface-energy parameter which determines whether the superconductor is Type I or Type II. Investigations of a magnetic hysteresis phenomenon which suggests the formation of vortices in molybdenum have also been carried out. Attempts to observe a sort of "Barkhausen noise" associated with the escape of trapped flux have thus far been unsuccessful, but equipment limitations have probably been responsible for the lack of success. For the future, further attempts will be made to observe the "Barkhausen noise" with more suitable electronic equipment. In this manner it may be possible to determine the amount of flux leaving a sample with trapped flux at one step. Measurements will be repeated on a sample of molybdenum of higher purity obtained from our Materials Science Laboratory. Work will also be extended to other superconductors.

Professor Houston and his students have been studying the energy losses in superconducting wires carrying large currents at audio frequencies, and they have been studying the mechanical forces occasioned by the motion of a superconductor through an inhomogeneous magnetic field. It has been established that the voltage-current characteristics of niobium-zirconium wires at audio frequencies can be described accurately by a model developed by Bean and by Kim. This model apparently applies quite well to the Type II superconducting alloy considered here. In contrast, lead, a Type I superconductor, does not obey the predictions of the model. In this work it has also been established that a
steady longitudinal magnetic field greatly increases the current density which can be supported by a superconducting wire. A model to explain this behavior has been developed.

Professor Houston and his students are also investigating the mechanical forces that act on a superconductor when it is moved in a magnetic field. For indium moving through a magnetic field concentrated in a fairly well-defined region, it has been found that a conservative force opposes the entry of the strip of indium into the field. The nature of this force depends on the thickness of the strip and on the sharpness of the region over which the magnetic field changes from zero to its maximum value. A viscous force has also been observed which is well described by an analysis due to Bardeen and Stephens for Type II superconductors. For the future it is proposed to analyze more fully the surface currents flowing on a sheet inserted into a magnetic field and to extend the experimental work to include Type II superconductors, through which the magnetic flux penetrates in a vortex structure.

D. Thermodynamics and Solid Surfaces—J. L. Margrave

Staff: R. Kobayashi, Professor of Chemical Engineering
J. L. Margrave, Professor of Chemistry
R. B. McLellan, Assistant Professor of Mechanical Engineering
Z. W. Salsburg, Professor of Chemistry
R. L. Sass, Professor of Chemistry

Theoretical, structural, thermodynamic, kinetic and optical characterizations of bulk solids and of the very important solid-gas interface at various temperatures and pressures are being provided by
use of computers, lasers, mass spectrometers, and a variety of other techniques.

In a theoretical study by Professor Salsburg consideration is being given to the role of anharmonic forces in solids at high pressures. The behavior of the molecular pair distribution function for a hard sphere solid in a face-centered cubic structure has been estimated. The analysis predicts an average force between pairs that is repulsive at high densities. The high-compression elastic behavior of both the two-dimensional rigid disk crystal and the three-dimensional hard sphere crystal has also been investigated.

Thermodynamic properties for ternary solutions containing both substitutional and interstitial solute atoms can be derived through use of a statistical model (see previous progress report). A computer analysis of available thermodynamic data for such solutions has shown that the theory gives excellent agreement with known thermodynamic behavior.

Structural data provide information that can be used for prediction of reaction mechanisms, and give insight into the details of atomic interactions in forming chemical bonds. Previous work by Professor Sass on the structure of cis-2-butene episulfone has indicated that the sulfone group dramatically affects the electronic structure of small ring compounds. This effect was also observed in the structure of dibenzothiophene-5, 5-dioxide. The structures of two other sulfone ring systems have now been examined by x-ray diffraction techniques. These are 2, 5-dihydrothiophene-1, 1-dioxide and 4-methylthiomorpholine-1, 1-dioxide. A complete set of data has been collected for both compounds and two- and three-dimensional Patterson functions have served to locate
the sulfur positions and parts of the remaining molecules. Work has not progressed to the stage where a statement can be made about the detailed geometry of either molecule.

Preliminary work on the structures of lead tetraacetate and dichlorobenzene diazo oxide is also in progress. A trial structure for the latter indicates that the crystals contain dimeric molecular complexes. The lead tetraacetate may also crystallize as a dimer or polymer.

Fundamental to the understanding of solids is a knowledge of their thermodynamic properties, over wide ranges of temperature and pressure. Both direct measurements on solids and studies of gas-solid interactions can provide such data. In one project under the direction of Professor McLellan thin Pd-Fe and Pt-Fe films are being prepared with isotopically-enriched iron containing Fe$^{57}$. Mössbauer second-order Doppler shift measurements will be made on these alloys to give information about the vibrational spectrum of the substitutional Fe solute atoms. This project is described in more detail in section B.

Gas-solid equilibria of many types are being investigated. For example, the equilibrium formation of gas-hydrates and the adsorption of methane, ethane and mixtures of these gases on silica gel are topics for one study by Professor Kobayashi. Professor Margrave and his students have been mainly concerned with the utilization of mass-spectroscopic techniques for the identification of molecular species and the derivation of thermodynamic properties. Bendix time-of-flight and magnetic mass spectrometry have been applied for studying transition metal fluorides and oxides. From measurements of the electron energies needed to fragment molecules in particular ways, it has been possible to deduce bond energies and related thermodynamic properties. Several
new molecules have been discovered including the species Si$_2$N for which no analogous molecule has been previously observed mass spectrometrically.

The subtle interrelationship between molecular species in condensed phases and in the gases equilibrated with these condensed phases has been explored by a careful study of the vapors over different crystalline modifications of SO$_3$. Only monomeric gas species were observed in spite of claims for complex polymers in the liquid and in the gas at high pressures.

An apparatus for the measurement of the thermodynamic parameters of interstitial atoms in dilute solution by a gas-solid equilibrium method is nearing completion.

Surfaces of solids can be characterized by optical, chemical and physical techniques. Final preparations are being made by Professors Rabson and Margrave for using a laser as a source of energy for vaporizing targets in a time-of-flight mass spectrometer. This should make possible the characterization of the surface of almost any solid. In addition to mass spectroscopic analysis, it is hoped that optical analyses may also be performed on the sample tested. (See section B).

The chemical and physical properties of surfaces can be grossly affected by optical irradiation. Thus, for example, the catalytic activity of magnesium oxide powders for the hydrogen-deuterium exchange reaction can be varied by irradiating the surface with selected ultra-violet radiation from a monochromator. Ultra-violet energies from 3 to 7 e.v. have been applied to MgO surfaces by Professor Leland and his students, and the first order rate constant produced at saturation at each frequency plotted as a function of the ultra-violet energy. The rate constant shows three well defined peaks at 4.9, 3.9, and 3.4 e.v. By comparison with studies of other investigators on optical
absorption, photoconductivity, and electron paramagnetic resonance in ultra-violet irradiated MgO, one can state quantitatively the energy of the electronic transitions affecting the catalysis and in some cases identify the physical nature of the excitation in the solid surface. This technique constitutes a reaction rate spectrometer to relate catalytic activity to electronic excitation.

Different chemisorbing and/or catalytically-reacting atmospheres can affect both the electrical conductivity and Seebeck EMF of compressed powders and single crystals. In this work by Professor Leland ZnO in compressed powder and in single crystal form has been exposed to O₂, CO, CO₂, and their mixtures. Although the magnitude of the electrical properties is quite different for the two solid forms, the response to changes in the atmosphere contacting the surface is quite similar. A model has been developed for the powder which permits application of single crystal theories to explain the behavior of the polycrystalline powder.

E. Thin Film Properties--H. C. Bourne, Jr.

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In thin ferromagnetic films a component of the magnetization perpendicular to the plane of the film produces a strong opposing or demagnetizing field. Hence, there is a strong tendency for the magnetization to remain in the plane of the film. However, under dynamic conditions the application of a switching field causes the magnetization to momentarily rotate out of the film plane, the consequent creation of
the demagnetizing field, and a resultant exceedingly rapid precessional motion about this field. Typical 80-20 Ni-Fe thin films may be switched in one or two nanoseconds with drive fields of the order of ten oersteds.

Another important property of these thin films is associated with the uniaxial symmetry produced when the films are evaporated in an applied magnetic field of the order of ten oersteds or higher. It is energetically favorable for the magnetization to be parallel (or anti-parallel) to the direction determined by the applied field during vacuum deposition. It is this binary character plus the ability to switch these films very rapidly that make them potentially very useful as computer memory elements, computer logic elements, and parametric device elements. Further possibilities such as nondestructive and very fast optical readout add to the already considerable interest. Polarized light reflected from the surface of the film provides contrast between oppositely magnetized states.

Finally, the film provides a very useful vehicle for exploring the properties and the parameters which influence the magnetic properties of materials. Increased understanding of the origins of the uniaxial anisotropy, the dynamic loss mechanisms, and the coercive force will certainly contribute to better design of magnetic devices in general as well as lead to very compact high-speed computers.

The most useful material for manufacturing thin film memory elements is an alloy of iron and nickel called permalloy. Since iron and nickel have different vapor pressures, the first problem attacked in this research was to study the degree of fractionation during vacuum vapor deposition of the alloy from a tungsten boat. For other reasons, the vacuum system had been designed with the substrates on
the end of an arm that could be rotated over the deposition source. Special long substrates were constructed so that they could be moved across the source by rotating the arm at a constant rate. The source was collimated by a slit aperture and the material ordinarily deposited through the thickness of a normal film was now extended along the length of the moving substrate. The vacuum was monitored during the deposition. The instantaneous thickness and composition were measured by the use of an electron probe microanalyzer, courtesy of Dr. David Mackay of the NASA Manned Spacecraft Center. It was observed that fractionation did occur and, hence, a normal film produced by small charge evaporation will have a composition gradient through its thickness. This gradient depends on the evaporation rate.

In addition two techniques useful to electron microscopists have been developed, and descriptions of these have been accepted for publication. (see Appendix I)

Two important mechanisms of flux reversal in ferromagnetic thin films have been identified in the wall motion or slow flux reversal region. One mechanism consists of the growth of relatively few domain tips parallel to the easy axis followed by the broadening of these stripe domains by parallel wall motion. The other consists of the propagation of many domain tips so that the film switches by the motion of an effective zig-zag wall moving parallel to the easy axis. The velocities and the mobilities of these walls have been measured in single and double layer films in thickness corresponding to cross-tie and Bloch walls in the single layer films and Neel walls in the double layer. Mathematical models of these processes predict switching times that are consistent with BH loop data.
APPENDIX I

Publications During The Period of This Report

A. Defect Structure and Mechanical Behavior

1. L. D. Whitmire and F. R. Brotzen
   "Effect of Impurities on the Plastic Flow of Molybdenum Crystals."
   Accepted for publication in the Proceedings of the International Conference on the Strength of Metals and Alloys, Tokyo, September, 1967.

2. L. D. Whitmire and F. R. Brotzen
   "The Effects of Deformation on the Electrical Resistivity of Molybdenum Single Crystals"
   Published Trans. of the Metallurgical Society, AIME, 239, 824, (1967).

3. J. M. Roberts
   "Relaxational Dislocation Damping Due to Dislocation-Dislocation Intersections with Application to Magnesium Single Crystals."
   Accepted for publication in the Proceedings of the International Conference on the Strength of Metals and Alloys, Tokyo, September, 1967.

4. J. M. Roberts
   "The Friction Stress Acting Upon Moving Dislocation as Derived from Current Microstrain Studies."
   Published Acta Metallurgica, 15, 411 (1967).

5. J. M. Roberts
   "A Note Concerning the Friction Stress Acting Upon Moving Dislocation as Derived from Current Microstrain Studies"
   Published Acta Metallurgica, 15, 569 (1967).

6. M. Yabe and J. M. Roberts
   "A Rapid and Accurate System for the Measurement of Ultrasonic Attenuation by the Pulse Method."
   Accepted for publication in Reviews of Scientific Instruments.

B. Electrical and Optical Properties

1. G. C. Jain and S. S. Li
   "Effect of Dimensions on the Efficiency of Radiant Energy Cells"

2. G. C. Jain and R. M. S. Al-Rifai,
   "Effects of Drift Field and Field Gradients on the Quantum Efficiency of Photocells."
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C. Magnetism and Superconductivity

"Measurements of Magnetization in Superconductive Molybdenum."

2. H. A. Blackstead and P. L. Donoho
"Microwave Absorption in Dysprosium Single Crystals."
Accepted for publication in the proceedings of the Sixth Conference on Rare-Earth Research.

3. F. Specht
"Anisotropy of the Indirect Exchange Interaction in the Rare Earth Metals."
Accepted for publication Phys. Rev.

D. Thermodynamics and Solid Surfaces

1. Z. W. Salsburg and W. Rudd
"A Modified Cell-Cluster Theory for the Solid State."
Published Physica, 32, 1601-1616 (1966).

2. R. D. Larsen and Z. W. Salsburg
"Cell-Cluster Development for the Pair Distribution Function. I."

3. R. D. Larsen and Z. W. Salsburg
"The Hard Sphere Solid: Pair Distribution Functions at High Density."

4. F. H. Stillinger and Z. W. Salsburg
"Elasticity in Rigid Disk and Sphere Crystals."

5. K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XX. Sublimation Pressures for TiF$_3$ and the Stabilities of TiF$_2$(g) and TiF(g)."
Accepted for publication J. Chem. Phys. (1967).
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6. K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XXI. The Heat of Atomization of Gallium Oxyfluoride."
Accepted for publication J. Inorg. and Nucl. Chem. (1967).

7. K. F. Zmbov
"Mass Spectrometric Isotopic Analysis of Chlorine by the Surface Ionization Method."
Accepted for publication Applied Spectroscopy, (1967).

8. J. D. McDonald and J. L. Margrave
"Mass Spectrometric Studies of Volatile Rare-Earth Chelates."
Accepted for publication J. Less-Common Metals (1967).

9. J. D. McDonald and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XVI. Sublimation of Chromium Trioxide."

10. P. J. Ficalora, J. W. Hastie and J. L. Margrave
"A Mass Spectrometric Study of the Reactions Between Gaseous Al and S2."
Accepted for publication Proceedings ASTM Meeting, Denver, May 19 (1967).

11. K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XI. The Sublimation Pressure of NdF3 and the Stabilities of Gaseous NdF2 and NdF."

12. Edited by J. L. Margrave
"Proceedings of Conference on Current and Future Problems in High Temperature Chemistry."
Publication No. 1470, National Research Council, Washington, D. C.

13. Edited by J. L. Margrave
"Characterization of High Temperature Vapors."
Accepted for publication (J. Wiley and Sons, New York).

14. K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Evidence for the Gaseous Si2N Molecule."

15. K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Studies of Rare Earth and Transition Metal Fluorides."
Accepted for publication Applications of Mass Spectrometry in Inorganic Chemistry, (1967) American Chemical Society.

17. J. D. McDonald, J. C. Thompson and C. H. Williams and J. L. Margrave. "Silicon-Fluorine Chemistry. V. Appearance Potentials and Thermodynamic Properties for Si$_2$F$_6$, Si$_3$F$_8$, Si$_4$F$_{10}$ and Si$_2$BF$_7$." Accepted for publication in Applications of Mass Spectrometry in Inorganic Chemistry (1967), American Chemical Society.


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5. K. R. Carson
"Preparation of Metal Foils by Mechanical Reduction."
Published Proceedings of the Twenty-Fifth Annual Meeting

6. K. R. Carson and M. L. Rudee
"An Improved Standard Specimen for Alignment of Electron
Microscopes."
Accepted for publication in Journal of Scientific Instruments.