William Marsh Rice University

Houston, Texas

Semi-Annual Status Report #19

on

NASA Research Grant ~~NsG-6-59~~ NGL-44-006-001

covering

Research on the Physics of Solid Materials

for the period

1 July, 1968 - 31 December, 1968

Under the Direction

of

F. R. Brotzen

H. E. Rorschach

and

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I. Introduction

The present strong interdisciplinary program in materials science and solid state physics and chemistry at Rice has been developed principally as a consequence of the support of the National Aeronautics and Space Administration, Grant NsG-6-59. The goals of this grant have been:

1. To promote the initiation and development of significant research programs by individual investigators and groups of investigators in the fields important for a fundamental understanding of solid materials. The distribution of funds has been determined by the significance and quality of the research, by its relevance to the goals of NASA, and by the prospect for interaction with related work at Rice and at other NASA laboratories. Both basic and applied work have been supported.

2. To increase the competence of students and staff in the disciplines related to an understanding of solid materials. Our objective is to develop a program of course work, seminars and research work that will prepare Ph.D. graduates in the broad field of materials as well as a specific research speciality so that they may assume responsible positions in research, development and applications.

3. To promote interdisciplinary cooperation wherever possible, so that the broadest possible perspective can be brought to each problem. The ultimate objective is to apply relevant insights of one area to another in which they have not been introduced.

To achieve the goals listed above, funds from this grant have been used to support the research of investigators from six university departments. As a consequence of this support, the accomplishments summarized below were made possible during the present reporting period.

1. The program involved 20 faculty members, 36 graduate students (9 foreign) and 9 postdoctoral fellows (7 foreign). The research results obtained by these workers is described in Section II. A total of 19 publication references to this work are given in Appendix I.

2. The interdisciplinary seminar program in solid materials was continued into its third year of operation.

3. The interdisciplinary course sequence in the physics of solids described in Status Report #17 was continued into its second year. This sequence has proven to be an important addition to our educational program in solid materials.

4. An organized program to encourage closer contact with investigators at NASA laboratories interested

in solid materials is continuing. Some of the Rice investigators have visited NASA laboratories, and this program will be expanded during the coming year. Further discussion of the accomplishments listed above is given in the following paragraphs.

The research reports given in Section II are presented in a form developed in the last few Status Reports. Research in progress has been divided into five areas, and a single staff member from that area has prepared the report on all related work. Our efforts have been directed toward improving the usefulness of these reports by presenting the basic aspects of the work in a form understandable to the non-specialist. In addition, over a period of time, each investigator will have the opportunity to present his work in some detail and to assess the work of others in his field.

The interdisciplinary seminar has continued into its third year on a weekly basis. The seminar has had a broad base; speakers have been drawn from faculty investigators, graduate students and outside specialists. Some of the seminar topics are listed below:

D. G. Pinatti - "Superconductivity of Molybdenum"

G. C. Schoeck - "Internal Friction due to Precipitates"

B. Dischler - "Spontaneous Distortion of a Paramagnetic Impurity in High-Symmetry Crystals"

C. T. Lee - "An Idealized Model for the Band Theory of Ferromagnetism"

M. L. Rudee - "Origin of Induced Uniaxial Anisotropy in Ferromagnetic Thin Films"

F. Tittel - "Optical Parametric Interaction in Crystals with Non-Linear Polarizability"

D. L. Davidson - "Plastic Flow in Molybdenum-Rhenium Alloys"

J. Hastie - "Thermodynamic Characterization of High-Temperature Liquids and Vapors"

T. S. Lundy - "Tracer Diffusion in Tungsten"

J. B. Coon - "Magneto-Acoustic Effects in Mercury"

B. Escaig - "Climb Kinetics of Frank Loops During Annealing in Pure Gold"

B. F. Brown - "New Perspectives in Stress-Corrosion Cracking Phenomena"

T. Courtney - "Mechanical Properties and Fracture in Composite Materials"

The second year of operation of the interdisciplinary course sequence in the physics of materials was begun. During the first semester, the following courses were given (enrollment is given in parentheses):

1. Introduction to the Solid State (14)
2. Dielectric and Optical Properties (6)
3. Imperfections and Mechanical Properties (8).

Several additional students audited these courses.

This program shows great promise. Expansion to include some further courses is under consideration, and this could be the first step toward a separate interdisciplinary graduate program in Materials Science.

In accordance with the program described in Status Report #18, efforts are continuing to establish significant contacts between investigators at Rice and those doing similar work in the NASA laboratories. During the past reporting period, the Lewis Flight Propulsion Laboratory, Cleveland was visited by Professor F. R. Brotzen, and Dr. J. D. Childress, NASA Electronics Research Center, Cambridge, visited the Rice campus. This program will be expanded during the coming year. Funds have been designated to provide travel expenses so that the individual investigators may be brought together where mutual interests exist.

A financial statement covering the period of this report is given in Appendix II.

II. Research Reports

A. Mechanical Properties and Defect Structure of Solids - M. L. Rudee

Staff: F. R. Brotzen - Professor of Materials Science
T. L. Estle - Professor of Physics
J. D. Ingram - Associate Professor of Mechanical Engineering
J. M. Roberts - Associate Professor of Materials Science
M. L. Rudee - Associate Professor of Materials Science
G. C. Schoeck - Visiting Professor of Materials Science
N. Soga - Assistant Professor of Space Science

It has long been recognized that most mechanical properties of solid materials are greatly modified by the defects that exist in their atomic or molecular lattice. Indeed, a perfect crystal, entirely free of lattice imperfections, would possess engineering properties which are entirely different from those of the real solid material. Among the various kinds of defects that are encountered in solids are point defects, such as "atomic vacancies" or "interstitials." Their number is greatly increased by radiation, such as one would find in a nuclear reactor, or by heat treatment or mechanical working. Another extremely important type of imperfection is the line defect or "dislocation." Dislocations are always present in solid materials, although their number may be increased by several orders of magnitude through plastic deformation. The number of dislocations in solid crystals and their distribution has a marked effect not only on the mechanical properties, such as strength and ductility, but also on the magnetic and electric behavior of solids.

For the understanding of the behavior of these defects in solid materials, a clear concept of the nature and properties of the perfect crystal is indispensable. Since the various defects create stress fields within the solid, they tend to interact with each other in an elastic manner. It is therefore evident that knowledge of the elastic properties of the solid is essential for the study of the interactions of defects. Moreover, a considerable amount of information can be gained by the application of the classical theory of elasticity, which ordinarily treats the solid as a continuum. Research on defect theory, therefore, lends itself particularly well to the kind of multidisciplinary approach that has been developed at Rice largely as a result of the NASA Materials Grant. A recent Conference on dislocation theory, organized by the National Bureau of Standards in Washington, D.C., which was attended by several members of the Materials Science Laboratory of Rice University, encouraged this approach.

A problem of fundamental importance, both from the technological and scientific points of view, is the understanding of the effect of alloy composition on the properties of metallic systems. At Rice, a study centers on the transition metals, which are of great commercial importance because of their abundance and potential high-temperature applications. The approach taken is to determine the imperfection behavior in these alloys as it is affected by the composition. Furthermore, through a concurrent series of investigations, the elastic properties of these systems are being studied in order to relate them to the electron configuration of the metallic solutions. This approach should eventually lead to a consistent picture whereby the mechanical behavior of these important alloys can be interpreted in terms of their known electron configuration.

One phase of this program has dealt with molybdenum-based rhenium alloys. The elastic constants of these alloys were determined over a wide range of temperatures by Professor F. R. Brotzen in cooperation with Professor N. Soga. It was possible, in a semi-quantitative way to correlate the elastic constants with the composition and the electron configuration of the alloys. Further research on the elastic behavior of these alloys was carried out by Professor N. Soga, who determined the pressure derivatives of the elastic constants of this system. He observed that the bulk modulus is not a unique function of the crystal volume, and that some ion-core interaction may exist in the pure molybdenum crystal. This interaction, however, tends to decrease as rhenium is added to the crystal.

Concurrent with the research on the elastic behavior of these systems, the dislocation structure in these crystals has also been studied. It was found that the addition of rhenium in small amounts tends to lower the flow stress of the crystals, while further addition of rhenium causes the flow stress to rise. One can therefore speak of "solution softening" although it is observable only below room temperature. On the basis of the experimental measurements of the various parameters of plastic flow for these alloys, it was concluded that two different dislocation mechanisms are operative during plastic flow. One of these prevails at lower temperatures and is characterized by a relatively high edge-dislocation mobility, while the other is associated with relatively high screw-dislocation mobility and exists at higher temperatures. The effect of the addition of rhenium to the molybdenum is to lower the temperature at which the transition from one mechanism to the other takes place. The details of this transition are being studied at present.

One of the features that affects the usefulness of many of the high-temperature metallic materials is their tendency to become brittle at a relatively low temperature. Professor J. M. Roberts has studied the temperature sensitivity of tantalum and molybdenum and their alloys with rhenium. He has studied the stress relaxation in these materials and observed that only very small amounts of deformation are required to produce a highly temperature-dependent "structural stress." After careful analysis of experimental data, it was shown that the completely relaxed stress has the same temperature dependence as the flow stress and lies between 80 and 95% of the flow stress. This finding suggests that the structural stress, and therefore the dislocation distribution in the material, adjusts itself to a new value at each temperature after strains of the order of 10^{-4}. These findings are also in agreement with earlier microcreep studies of molybdenum single crystals carried out by Professors J. M. Roberts and F. R. Brotzen.

One of the characteristic properties of most solid materials is that the material tends to become stronger as it is deformed. Although much is known about work hardening of metals and alloys, there are many specific aspects that have not yet been clarified. Professor G. C. Schoeck, who has been visiting the Materials Science Laboratory of Rice University during the academic year 1968-69, has been concerned with work hardening of alloys that possess long-range order. Specifically, a theory for the deformation of Cu_3Au crystals was developed by Professor Schoeck, according to which work hardening in these ordering systems is related to the drag effect of so-called "anti-phase domain tubes." Professor J. M. Roberts and his students are presently trying to check experimentally the predictions of this theory of the slip-line structures in the ordered and disordered samples. The relations that exist between work hardening effects and both the microplasticity and the anelastic back strain are also being tested.

In all of these projects extensive use has been made of the electron-microscope facility, which is under the direction of Professor M. L. Rudee. The equipment is also used in projects which are not directly related to the study of mechanical properties and lattice defects, notably the investigation of ferromagnetic thin films. Close cooperation with the Department of Biology has also created some other interesting projects in which the electron microscope is used extensively.

As was mentioned earlier, considerable knowledge of the behavior of solid materials can be gained when the material is viewed as a continuum. Professor J. D. Ingram and his students have been concerned with a general method for the solution of systems of quasi-linear partial differential equations. This method involves mathematical transform techniques along characteristics and yields a non-linear system of integral equations which can be solved numerically. The group has used this method for the study of properties of non-linear elastic solids by means of their dynamic response. So far, this method has been successfully applied to a one-dimensional non-linear string and to certain non-linear elasticity problems. An experimental study of the non-linear string is also in progress.

For a better understanding of point imperfections, mostly in the form of impurity ions, spectroscopic studies in non-metallic crystals, such as alkali halides, have been carried out by Professor T. L. Estle and his students. Through these studies, a detailed atomic-scale description of isolated point imperfections can be obtained. One of the techniques employed is that of the recently discovered paraelectric resonance, which was discussed in the preceding semi-annual status report. Professor Estle has been able to show the importance of internal strains on the paraelectric resonance by combined theoretical and experimental studies on lithium-doped potassium-chloride crystals. Paraelectric resonance has also been observed in lithium diffused into sodium chloride crystals. Another method used for the better understanding of point imperfections is electron-paramagnetic resonance. This technique has been applied to strontium-chloride crystals containing lanthanum ions. The observations serve as an excellent example of the dynamic Jahn-Teller effect. This work is discussed further in section C.

B. Magnetism and Superconductivity - T. L. Estle

Staff: H. C. Clark - Assistant Professor of Geology
P. L. Donoho - Professor of Physics
T. L. Estle - Professor of Physics
H. E. Rorschach - Professor of Physics
G. T. Trammell - Professor of Physics

The research in this field at Rice has broadened since the last report (#18). In addition to the studies of rare-earth metals and superconductivity, there is now research on isolated paramagnetic ions by electron paramagnetic resonance and on the magnetization of ferromagnetic materials found in natural rocks (paleomagnetism).

As part of their attempt to understand point imperfections in which vibrational properties play a major role, Professor T. L. Estle and his students have been studying the dynamic Jahn-Teller effect of impurities having E ground states. These states have a two-fold orbital degeneracy. Hence they are unstable against a symmetry-lowering distortion. This distortion therefore occurs spontaneously, and its occurrence is called the Jahn-Teller effect. The simplest behavior occurs for large distortions which produce a lower symmetry locally and a consequent modification of the electronic energy level diagram. If the distortion is not large enough to approach this limit, then the states of the system must be described by vibronic functions, i.e. functions depending on both the electronic and the nuclear coordinates. This phenomenon is called the dynamic Jahn-Teller effect.

The dynamic Jahn-Teller effect is being studied by electron paramagnetic resonance in $SrCl_2$ single crystals containing about 0.1% La^{2+} ions. La^{2+} has a single electron. Somewhat surprisingly it is a 5d electron rather than 6s or 4f. A single electron normally produces a single isotropic electron spin resonance line (neglecting hyperfine structure). In contrast, two anisotropic lines are observed with a remarkable temperature dependence. The dynamic Jahn-Teller effect is responsible for these results.

In order to understand both resonant and nonresonant absorption of microwaves in dysprosium and other rare earth single crystals, Professor P. L. Donoho and his students have been calculating spin wave dispersion relations for dysprosium. Spin waves are important in ordered magnetic materials because they are the excited states of lowest energy. Their wave-like character reduces the contribution of exchange to the energy. The gradual variation of the orientation of the spins results in larger contributions to the energy from anisotropic terms. The large magnetostriction of the rare earths and the hexagonal anisotropy of the dysprosium were shown to produce a strong angular dependence of the resonance frequencies. The nonresonant absorption was found to arise from a new component of the magnetostriction.

Complementing the experimental work is the theoretical work of Professor G. T. Trammell and his students on the effects of anisotropic exchange on the spin wave spectrum in the rare earths.

The weak magnetization of ferromagnetic materials in rock is being studied by Professor H. C. Clark and his students. Virtually all rocks formed from a melt containing ferromagnetic materials will acquire a permanent magnetization as the rock cools through its Curie temperature. This permanent magnetization serves as a record of the intensity and direction of the magnetic field present at the time the rock was formed. These rocks will contain ferromagnetic materials of various compositions, which will have various grain sizes, and they will also have experienced complicated thermal histories. Nevertheless it is possible to extract the desired information with reasonable certainty.

Studies have been principally directed toward the investigation of samples of Precambrian granites (1 billion years old) from the Llano region of Texas. The object is to study the factors influencing the decay of the remnant magnetization in exceptionally old rocks. The magnetization was somewhat stronger than expected, suggesting that the earth's magnetic field was somewhat stronger one billion years ago than it is now. The direction of the magnetization showed the "North" magnetic pole to lie south of the equator in the eastern Pacific at that time. This agrees with most of the few reliable pole determinations from other parts of the world.

Professor H. E. Rorschach and his students have been studying the superconductivity of molybdenum. Superconductors can be classified as being of two kinds: type I or type II. Type I superconductors exclude magnetic flux from the material except for a thin layer near the surface. For type II superconductors, flux penetrates in a regular way so that normal regions with high flux are surrounded by superconducting regions. A convenient parameter for characterizing this behavior is the Ginsberg-Landau Kappa factor. Is is proportional to the upper critical field in type II superconductors and extrapolates in the type I region as the supercooling field. It is currently interpreted as a quantity that depends only on the basic electronic properties of a superconductor. Studies of supercooling and flux penetration have been made as a function of annealing time for very pure single crystals of molybdenum. The Kappa factor decreased remarkably following long high vacuum anneals, showing the importance of extended defects in nucleating superconductivity. It may be possible to reduce further the Kappa factor in Mo by additional purification and annealing. These results raise some important new questions concerning the fundamental significance of the Kappa factor.

C. Electrical and Optical Properties - L. E. Davis

Staff: L. E. Davis - Assistant Professor of Electrical Engineering
T. L. Estle - Professor of Physics
T. A. Rabson - Associate Professor of Electrical Engineering
F. K. Tittel - Associate Professor of Electrical Engineering
G. T. Trammell - Professor of Physics

An understanding of the electronic structure of solids, and the interactions between solids and oscillating electric fields, is necessary for the application of solid-state phenomena to new devices. The research to be described in this section involves electric fields oscillating at frequencies in the range 10^9 Hz to 10^{20} Hz, which, in turn, implies widely differing experimental techniques.

(1) Microwave Properties (2×10^9-4×10^{10} Hz)

The work of Professor T. L. Estle in the Physics Department on Paraelectric-Resonance Spectroscopy has been published [Phys. Rev., Dec. 1968], and he is presently studying ferroelectric materials. The objective is to explore the possibility of observing ferroelectric resonance in low-transition-temperature materials. It is hoped that it will be the cooperative version of paraelectric resonance in analogy to ferromagnetic resonance and electron paramagnetic resonance. In paraelectric resonance, electric dipole transitions between energy states of a paraelectric imperfection in a crystalline solid are stimulated by an oscillating electric field. In contrast to electron paramagnetic resonance for which the gyromagnetic coupling is the basis for resonance, quantum mechanical tunneling and the Stark effect are the essential features for paraelectric resonance. The experimental work cannot be started until there is more complete understanding of the simple phenomena involved in paraelectric resonance. Theoretically some brief attempts to include tunneling in the description of ferroelectrics and to investigate the possibility of spin-wave-like excitations were somewhat encouraging. It appears likely that very high microwave frequencies will be required to observe ferroelectric resonance.

Professor L. E. Davis and his students in the Electrical Engineering Department are working on the theory and applications of microwave propagation in gyrotropic media. Examples of such media are gaseous and solid-state plasmas and ferrites immersed in a static magnetic field. The interest in these materials arises from their ability to exhibit non-reciprocal (NR) propagation, i.e. different (complex) propagation constants in antiparallel directions. Only these materials can be used to develop the passive NR components, e.g. circulators, isolators and phase shifters, which are now widely used in microwave spectroscopy, radar systems and microwave links. As a result of this work, (1) H-plane waveguide circulators are now available that have relative bandwidths double the bandwidths previously available (2) a general theory of matching networks for NR devices is available (3) a preliminary theoretical model of microwave propagation in semiconductors has explained the gross features of some unexplained experimental results in the literature.

Professor T. A. Rabson and his students are investigating microwave generation in bulk semiconductors. The purpose is to study ways of frequency tuning and modulating Gunn oscillators, and to study experimentally the influence of material parameters on the electrical characteristics of the oscillators. The original Gunn Effect was the coherent microwave output observed when the d.c. bias field applied across a randomly oriented n-type sample of GaAs exceeded a critical field of several kV/cm. The frequency of the output was approximately equal to the inverse of the carrier transit time. The instability has been explained in terms of a two-valley conduction band model, in which the electrons in the lower valley have light mass and high mobility while those in the upper valley have heavy mass and low mobility. Thus, as the bias field is increased, there is a range where the current decreases, i.e. a range of negative conductivity. This negative conductivity leads to an electrical breakup of the crystal into alternating traveling domains of high and low fields, accompanied by an alternating current. The development of Gunn oscillators has provided an extremely compact source of microwave power that will have applications to small portable radar, communications systems, radio astronomy and elsewhere. But the theoretical frequency limit has not yet been attained, and the full potential of these devices will not be realized until better means of tuning them over a wide band of frequencies are developed and simple modulation techniques are invented.

(2) Optical Properties (10^{14}-10^{15} Hz)

Professor F. K. Tittel and his students in the Electrical Engineering Department are studying optical parametric processes. The primary objective is to build an efficient and versatile continuously tunable CW parametric oscillator at optical frequencies using both $LiNbO_3$ and $Ba_2NaNb_5O_{15}$ crystals as the nonlinear medium. A versatile optical system is being constructed for these investigations. Every effort is being made to use computer techniques to optimize the design, and this has been particularly useful in selecting the best parametric interaction scheme and evaluating different frequency tuning mechanisms. Another aspect of this parametric interaction investigation is the possibility of frequency conversion from infrared to microwave frequencies. Such an investigation may lead eventually to tunable sources in the difficult part of the spectrum between microwaves and the far infrared, i.e. frequencies in the range 10^{11}-10^{13} Hz. Such sources would be of great interest to spectroscopists.

(3) Gamma-Ray Properties ($f \sim 10^{19}$ Hz)

Professor G. T. Trammell and his students in the Physics Department have published several papers on "Mössbauer Optics," and this work is being extended to consider applications and also the question of Gamma-Ray sources. Transitions between low-lying nuclear states of long life are responsible for the emission and absorption of gamma rays of sharp energy. In addition, if the recoil momentum is taken up by the entire crystal, there will be no shift in the frequency of the emitted radiation. These are Mössbauer gamma-rays. The first paper develops the fundamental theory of Mössbauer Diffraction and the second paper treats in detail Bragg reflection, Bormann transmission, critical reflection, and off-Bragg transmission. Other papers have discussed tests for the time-reversal invariance of nuclear interactions utilizing Mössbauer gamma rays and the interference of electronic and nuclear resonance absorption. Finally, in a paper entitled "Quantum Limitations on Molecular Microscopy," it has been shown that any attempt to image an atom in a molecule will result in drastic damage during the time of the observation (except, possibly, for the very simplest molecules).

D. Thermodynamics and Solid Surfaces - J. W. Hightower

Staff: J. W. Hightower - Associate Professor of Chemical Engineering
R. Kobayashi - Professor of Chemical Engineering
T. W. Leland - Professor of Chemical Engineering
J. L. Margrave - Professor of Chemistry
R. B. McLellan - Assistant Professor of Materials Science
M. L. Rudee - Associate Professor of Materials Science

A multi-departmental program sponsored by the NASA Materials Grant at Rice has been aimed at providing a deeper insight into the nature of several different kinds of solids.

The experimental work which has involved kinetic or thermodynamic measurements will be presented in this report under two headings depending on whether the work deals primarily with solid surfaces or with the bulk properties of solids.

1. Solid Surfaces

Several investigators in the chemistry and chemical engineering departments have been examining the nature of both physical and chemical interactions which occur between gas phase substances and solid surfaces. These will be listed in the order of increasing interaction energy, i.e., from physical adsorption, to chemisorption and catalysis, to gas-solid chemical reactions (ablation).

a. The Nature of Methane Adsorption on Fused Glass Beads

Gas chromatography is usually applied to the separation of gases and to chemical analysis. However, a group headed by Professor R. Kobayashi has developed a method for using a perturbation chromatographic technique to measure directly several important physicochemical properties during physical adsorption of gases on solid materials. Basically, this technique involves flowing a stream of some gas (e.g., methane, $C^{12}H_4$) at a fixed temperature and pressure through a bed packed with a few grams of the solid material (e.g., fused glass beads) until a steady state is attained. Small pulses of the same material but containing a distinguishing radioactive isotope (e.g., methane, $C^{14}H_4$) are then injected into the stream, and their retention times are measured by an ionization detector in the effluent stream. Pulses of other gases may also be injected under a range of conditions, and from their retention times several thermodynamic parameters may be determined under conditions of flow equilibrium.

Although the technique may be used to study Gibbs adsorption and absolute adsorption, it has been used most effectively to obtain precise values for two parameters previously unattainable, namely, the amount of adsorption and the free gas volume, V_g, in a column packed with a gas-adsorbing solid. Because conditions of very high dilution are readily attainable by perturbation chromatography, this method has been used to determine infinite dilution partitioning characteristics with a minimum of measurements.

b. A Study of the Irradiation Effects on Catalytic Properties of Magnesium Oxide

One of the significant uncertainties in the field of heterogeneous catalysis centers around the relationship between catalytic activity and solid state properties of the catalyst. In a series of elegant irradiation experiments, Professor T. W. Leland's group has successfully correlated the irradiation enhancement of the rate of H_2-D_2 equilibration with certain electronic transitions which can occur between the valence band and impurity energy levels in the bulk of magnesium oxide.

At room temperature, partially dehydrated MgO is not a very active catalyst for the H_2-D_2 exchange reaction. However, when this material is subjected to ultraviolet irradiation, the catalyst becomes quite active; this has been known for several years. What was not known is that only <u>certain specific</u> UV frequencies are effective for this activation. By using a variable monochromator, the Rice group was able to irradiate the sample with very narrow energy bands and note the effect on the reaction rate. Three "peaks" in the "reaction rate spectrum" were observed at 4.0 ev, 4.9 ev, and 5.7 ev, and these were attributed respectively to (1) OH° formation by excitation of an electron from OH^- to a surface impurity, (2) OH° production on the surface by excitation to a surface impurity such as Fe^{+3}, and (3) formation of OH° by donation of an electron to a V_1 center formed near the surface. These OH° groups served as center for the catalysis. The greatest rate enhancement was well over an order of magnitude with the 4.9 ev irradiation.

One of the advantages of this technique is that the catalyst samples can be reused. After each irradiation and reaction, the enhancement effect could be thermally erased by annealing at about 300°C for a few minutes, after which treatment the rate returned to the un-enhanced value.

On the basis of these results it was possible to draw a detailed band diagram of the electronic transitions which occur in the surface region of magnesium oxide and to understand more fully the nature of the catalytic properties of this insulator.

c. Surface Interactions on Ferrite Catalysts

A majority of the commercially important chemical butadiene manufactured in this country is made by the catalytic oxidative dehydrogenation of butene. Although this reaction is known to occur over several materials having spinel-type structures (e.g., $MgFe_2O_4$, $ZnFe_2O_4$, etc.), very little is known about the actual mechanisms of the surface interactions which may be involved. A group under Professor J. W. Hightower has undertaken some isotopic tracer studies on this system in an attempt to correlate some of the catalytic activity with certain structural properties of the solid.

Magnesium ferrite was chosen as a representative solid because it is easy to obtain, is in general fairly well crystallized, may potentially have some interesting magnetic properties, is readily amenable to such elegant techniques as Mössbauer spectroscopy, and is catalytically active. The oxidative dehydrogenation of butenes to butadiene filled the requirements of a test reaction in that it involves interaction of both organics and inorganics with the solid, and all compounds are easily handled analytically and afford the possibility of using both stable and radioactive isotopic tracer techniques. Furthermore, competition between the desired oxidative dehydrogenation reaction and the undesired but thermodynamically more favorable total oxidation reaction provides an additional dimension by which catalytic selectivity can be studied as a function of solid state properties.

Initial work involved setting up a recirculation reactor system associated with a gas-liquid chromatography apparatus in which reaction products could be separated and trapped for subsequent analysis in a mass spectrometer or radioactivity assaying device. All this has been accomplished, and conditions for studying the reaction have been defined.

One surprising result is that the n-butenes are not isomerized to equilibrium at temperatures in the region 300 to 400°C, even though oxidative dehydrogenation occurs rapidly under these conditions. This led the investigators to suspect that interaction of the olefin with the surface was the rate-limiting process and that the most difficult part of the reaction was cleavage of two C-H bonds. A large primary kinetic isotope effect ($k_H/k_D \sim 2$ to 3) when 1:1 mixtures of perdeuterio trans-2-butene (C_4D_8) and regular trans-2-butene (C_4H_8) were reacted over the catalyst confirmed this suspicion. There was no evidence of any intermolecular scrambling of the H and D atoms in either reactants or products. Before the nature of the active surface sites can be explored, it is necessary to determine pathways through which the reactions occur. For example, some total oxidation to CO_2 and H_2O does occur, but it is not apparent whether this arises from direct oxidation of the butene (path one) or subsequent oxidation of the butadiene (path two), viz.:

$$\text{Butene} + O_2 \rightarrow \text{Butadiene} + H_2O$$

$$\downarrow \qquad\qquad\qquad \downarrow \text{Path two}$$

$$\text{Path one} \rightarrow CO_2 + H_2O$$

Addition of traces of radioactive C^{14}-butadiene to the reactant butene has helped resolve this question, since quantitative analysis of radioactivity in the CO_2 identifies its source. Preliminary experiments indicate that both pathways are significant.

The selectivity (butadiene vs. CO_2 formation) appears to be a function of catalyst pretreatment, and it changes (as does the total activity) with successive runs over the same reactivated sample. Deactivation, or poisoning, appears to be an irreversible process and may indicate some changes in the solid structure. X-ray diffraction patterns show minor but consistent differences. For example, small X-ray lines which may correspond to α-Fe_2O_3 are present in the active catalyst, but are absent when the catalytic activity and selectivity are low after prolonged use. It is possible that such non-stoichiometric regions may serve as defect centers on which the desired catalysis occurs. Mössbauer spectra are now being run on the same samples which have been subjected to various pretreatments.

d. High-Temperature Interactions between Gases and Condensed Phases

Thermodynamic and kinetic parameters must be determined with precision in order to explain the behavior of materials in the presence of reactive gases, particularly at high temperatures. Professor J. L. Margrave and co-workers have applied mass spectrometry, laser excitation, high pressure infrared, and levitation calorimetry to provide some of this much needed information.

A variety of mass spectrometric studies of gas-solid equilibria have been carried out in the time-of-flight and magnetic mass spectrometers. The collection of thermodynamic data for transition metal species is very extensive, and sufficient information has now been obtained to provide the basis for theoretical calculations using available computer programs and modern quantum mechanical techniques. Current efforts are directed toward the use of laser excitation and time-resolved mass spectrometry for study of kinetics and mechanisms of gas-solid reactions.

Studies of high pressure phenomena have been continued with special emphasis on the structure determinations for high pressure borate phases and for the high pressure modification of CF. A computer program for indexing powder patterns of low symmetry has been obtained, and the unit cell for CF has been determined as orthorhombic. A detailed study of the arrangement of atoms in the unit cell is in progress. The high pressure infrared diamond cell has been received, and experiments with it are being prepared. Initial interest will be in the effects of pressure on the positions of electronic energy levels and on vibrational frequencies.

Reactions of elementary boron with copper, gallium, tellurium and several other elements have been carried out and some new phases identified.

Properties of liquid metals at high temperatures are currently being investigated by use of levitation calorimetry. Heats of fusion for copper, titanium, cobalt, nickel and platinum have been measured.

2. <u>Bulk Solids</u>

Two projects in the Materials Science Laboratory have been aimed at determining some of the kinetic and thermodynamic properties of solid solutions and alloys.

a. Thermodynamics and Diffusion Kinetics of Solute Atoms in Solid Solutions

The purpose of this research under Professor R. B. McLellan is to investigate the thermodynamic parameters of solute atoms in solid solutions, with special emphasis on the total energy and vibrational entropy in solution. These parameters may then be compared with values obtained from theoretical models which predict both the thermodynamics of solutions and the diffusion kinetics of the solute atoms.

Measurements at very low temperatures of the free energy of carbon atoms in bcc iron have been made. The thermodynamics of carbon solutions in copper, gold, and silver have also been measured over a large temperature range. These solutions were found to obey simple (regular) mixing statistics.

Preliminary results have been found for the diffusivity of carbon in the high temperature bcc phase of iron (α iron) at 1450°C. More data are currently being obtained on this system.

Theoretical treatments of vacancy formation in metals, diffusion of interstitial atoms, and ternary solid solutions have been devised, shown to be in accord with published data, and accepted for publication.

b. The Application of the Temperature Dependence of the Mössbauer Resonance to Study the Thermodynamic Properties of Alloys

Both the position and strength of the Mössbauer resonance are related to the vibrational behavior of the resonant species, and information about the lattice dynamics can be extracted from the temperature dependence of the Mössbauer effect. The unique strength of this technique lies in its application to rather dilute solid solutions for which most other methods would monitor only the major constituent. The objective of this research, which is directed by Professors R. B. McLellan and M. L. Rudee, is to study the vibrational properties of Fe as the minor constituent in a dilute solid solution. In particular, the excess vibrational entropy of Fe in Pt can be obtained in this way. Since the total entropy is known from the work of others, an unusually complete thermodynamic description of this system should be possible. The success of this experiment depends on sample temperature control. A helium or nitrogen flow cryostat with appropriate gamma-ray-transparent windows has been constructed for this purpose. Spectra have been recorded and a computer program to characterize the peaks has been acquired and debugged. The first runs have the proper qualitative temperature dependence, but inaccuracies in the voltage reference for the velocity drive must be eliminated in order to reduce the scatter and make a quantitative analysis more meaningful.

E. Thin Magnetic Films - M. L. Rudee

Staff: H. C. Bourne, Jr. - Professor of Electrical Engineering
T. Kusuda - Visiting Associate Professor of Electrical Engineering
M. L. Rudee - Associate Professor of Materials Science

The properties of magnetic thin films have been closely scrutinized during the past decade by a large number of investigators; over 1500 publications have resulted. This research effort was motivated by three considerations. First, studies of thin films have contributed to a better understanding of some aspects of the physics of magnetism. Second, some of the magnetic properties are so sensitive to the structure of the films that they can be used to investigate thin film properties. Third, magnetic thin films give promise of utility in certain devices.

The most common practical application studied thus far is the thin film computer memory. To be useful, a magnetic film must compete with the common core, a bistable element that consists of a toroid of magnetic oxide. A device having the necessary square B-H loop can be obtained by producing a metallic film with a magnetic field (typically about 50 Oe.) applied in the plane of the film during its growth. Almost any deposition technique can be used, but the discussion here will consider only vapor deposition on to flat substrate.. The applied field defines a direction of magnetization during the deposition process. It is found that this direction is thereafter the lowest energy state for the film's magnetization and is referred to as the "easy axis." To switch the sense of the magnetization, an energy barrier perpendicular to the easy axis (the "hard axis" direction) must be surmounted. This creates a bistable element.

The impetus for studying thin film memory elements is that the direction of magnetization, and hence the binary information, can be switched faster than in core memories. In addition, there is promise that the price and packing density can be made more attractive. Despite the effort that has been expended on thin film memory elements, many questions remain unanswered, and they remain a fruitful area for research.

The research on magnetic thin films at Rice has centered in groups in two academic departments. In Electrical Engineering, Professor H. C. Bourne and his students have been studying the dynamics of the flux reversal process by both indirect sensing and by direct observation. Recently they have investigated a problem of great importance in memory applications. If memory elements are packed fairly closely together, repeated stray field pulses from the switching of nearby elements can have a detrimental effect even though the pulses are below the normal threshold for switching or are in the hard axis direction. To understand this phenomenon, films of 81% Ni and 19% Fe have been subjected to very fast pulses (rise time of less than 10 n-sec.) along the hard axis. To describe the results, the following model has been developed. A fast pulse causes the magnetization on either side of a domain wall to switch coherently to the new equilibrium configuration before the wall can move. This configuration produces a demagnetizing field in the wall about which the magnetization in the wall precesses. This precession causes an irreversible step change in wall position, and thereby repeated pulses can destroy the information state of an element. Quantitative agreement between theory and experiment is gratifying. In the future more detailed experiments are planned to test the details of the model.

In Materials Science, Professor M. L. Rudee and his students have been studying the relation of magnetic properties to structural aspects of films. The structure of the film has been altered by changing the composition and by annealing. The magnetic properties measured are the coercive force and the magnitude and angular dispersion of the uniaxial anisotropy; the structure has been characterized by transmission electron microscopy. During the reporting period, two experimental efforts have been in progress. One has contributed to the understanding of the origin of the uniaxial anisotropy. One of the mechanisms proposed to explain the anisotropy depends on the strength of the mechanical bond between the film and the substrate. Films of a range of compositions have been prepared on substrates coated with a silicone grease that prevents any adhesion. The comparison between the magnitude of the anisotropy in these special films and films prepared in the normal way has contributed to the understanding of the origin of the anisotropy.

In another series of experiments the effect of annealing on both the magnitude and dispersion of the anisotropy is being studied in films of a wide range of compositions. The changes in the grain size produced by the various annealing treatments are also being measured. It has been observed that the magnitude of the anisotropy is largely reversible, while the dispersion is only partially recoverable. It is believed that by measuring the degree of reversibility as a function of composition, as well as studying the kinetics and the grain size, a quantitative test of the theories of the dispersion can be achieved.

APPENDIX I

Publications during the Period of this Report

A. Mechanical Properties and Defect Structure of Solids

1. L. D. Whitmire and F. R. Brotzen
   "Effects of Impurities on the Plastic Flow of Molybdenum Crystals."
   Supp. Trans. Japan Institute of Metals 9, 867 (1968).

2. D. L. Davidson and F. R. Brotzen
   "Elastic Constants of Molybdenum-Rich Rhenium Alloys in the Temperature Range -190°C to +100°C."
   Journal of Applied Physics 39, 5768 (November, 1968).

3. J. M. Roberts
   "Relaxational Dislocation Damping due to Dislocation-Dislocation Intersections with Application to Magnesium Single Crystals."
   Supp. Trans. Japan Institute of Metals 9, 69 (1968).

4. T. L. Estle
   "Paraelectric Resonance Spectroscopy."
   Phys. Rev. 176, 1056 (1968).

B. Electrical and Optical Properties

1. J. P. Hannon and G. T. Trammell
   "Mössbauer Diffraction II: Dynamical Theory of Mössbauer Optics."
   Accepted for publication in The Physical Review.

2. J. P. Hannon and G. T. Trammell
   "Tests of Time Reversal Invariance of Strong Interactions Utilizing the Mössbauer Effect."
   Phys. Rev. Letters 21, 726 (Sept. 1968).

3. J. P. Hannon and G. T. Trammell
   "Interference of Electronic and Nuclear Resonance Absorption for Mössbauer El Gamma Rays."
   Accepted for publication in the Physical Review (April, 1969).

4. T. K. Gaylord, P. L. Shah and T. A. Rabson
   "Gunn Effect Bibliography."
   I.E.E.E. Transactions on Electron Devices ED-15, 777-788 (1968).

C. Magnetism and Superconductivity

D. Thermodynamics and Solid Surfaces

1. S. Masukawa and R. Kobayashi
"Adsorption Equilibrium of the System Methane-Ethane-Silica Gel at High Pressures and Ambient Temperatures."
J. Chem. Eng. Data 13, 197 (1968).

2. S. Masukawa and R. Kobayashi
"Experimental Determinations of the Molar Heat and Entropy of Adsorption and the Activity Coefficient of the Adsorbed Phase for the Methane-Ethane-Silica Gel System."
Accepted for publication in A. I. Ch. E. Journal (Summer, 1969).

3. C. G. Harkins, W. W. Shang, and T. W. Leland
"Relation of Catalytic Activity on MgO to its Electron Energy States."
J. Phys. Chem. 73, 130 (1969).

4. J. W. Hastie, P. J. Ficalora, and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures, XXVII. Reactions of Aluminum Vapor with $S_2(g)$, $Se_2(g)$, and $Te_2(g)$."
J. Phys. Chem. 72, 1660 (1968).

5. P. Ficalora, J. C. Thompson, and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures, XXVI. The Sublimation of SeO_2 and SeO_3."
Accepted for publication in J. Inorg. and Nuclear Chem.

6. J. A. Sprague and R. B. McLellan
"Thermodynamics of Iron-Carbon Solutions."
Trans. AIME 242, 733 (1968).

7. D. H. Coplin, J. E. McGinness, and R. B. McLellan
"A Statistical Model for Ternary Solid Solutions Containing both Substitutional and Interstitial Solutes."
J. Jap. Inst. Metals (March, 1969).

8. W. A. Oates and R. B. McLellan
"The Darken-Alcock-Richardson Equation for Ternary Solid Solutions."
Trans. AIME 242, 1472 (1968).

9. W. W. Dunn, R. B. McLellan, and W. A. Oates
"The Solubility of Carbon in Solid Nickel and Cobalt."
Trans. AIME 242, 2129 (1968).

10. R. H. Siller, W. A. Oates, and R. B. McLellan
"The Solubility of Carbon in Palladium and Platinum."
J. Less Common Metals 16, 71 (1968).

E. Thin Film Properties

1. H. C. Bourne, T. Kusuda, and C. H. Lin
"Bloch Wall Motion in Ferromagnetic Films Excited by Fast-Rising Hard-Axis Pulses."
Accepted for publication in Journal of Applied Physics (February or March, 1969).

APPENDIX II

Financial Report

NASA Grant NsG-6

	Report of Expenditures For the Period 7/1/68 to 12/31/68		For the Period 5/1/59 to 12/31/68	
Salaries				
Professional	$74,408.76	$	$719,736.43	$
Students	5,079.96		433,914.63	
		79,488.72		1,153,651.06
Overhead				
At 50% of Salaries included in the 1st $1,150,000 of Expenditures			235,429.10	
At 25% of Direct Costs not to exceed $120,000 of next $600,000 Expenditures			120,000.00	
At 20% of Direct Costs		26,930.85	138,114.16	
				493,543.26
Expendable Supplies and Materials	33,836.74		456,969.95	
Minor Equipment	6,101.47		152,853.05	
		39,938.21		609,823.00
Major Equipment		15,227.34		321,652.30
Commitments Outstanding				
Salaries	12,484.97			
Materials & Supplies	6,709.31			
Equipment	3,436.10			
Overhead for Commitments	4,526.08			
		27,156.46		27,156.46
Totals		$ 188,741.58		$ 2,605,826.08

APPENDIX II (CONT'D)

Financial Report

NASA Grant NsG-6

	Report of Expenditures For the Period 7/1/68 to 12/31/68	For the Period 5/1/59 to 12/31/68
Major Equipment		
High Pressure Diamond Cell with heating element, Type II	$ 2,180.00	
Precision Lock-in Amplifier (Demonstration Unit) Model HR-8 S/N 600 w/ low impedance transformer input preamplifier (w.l, plug female, Cannon #XLR-3-11-C) (Demonstration Unit) Model Type B, S/N 433 (10% discount for demonstration unit)	2,115.00	
Mössbauer Driver S/N 2424 Model No MD-2	1,550.00	
Hasselblad 500-C Camera TR#81939, w/80mm lens #4491064 and 12X back TR121682 complete with accessories	4,177.34	
Precision lock-in amplifier, Model HR-8, S/N 2079 w/low impedance transformer input preamplifier w/female plug Cannon #XLR-3-11C Type B, S/N 670	2,350.00	
Pressure Balance, Aminco 20,000 psi, pressure range 500 to 20,600 psi w/46-19330 hand operated pressure generator	2,855.00	
	$ 15,227.34	