William Marsh Rice University

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covering

Research on the Physics of Solid Materials

for the period

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Under the Direction

of

F. R. Brotzen

H. E. Rorschach

and

M. L. Rudee

I. Introduction

A program in materials science and solid state physics and chemistry has been developed at Rice University as a consequence of the support of the National Aeronautics and Space Administration. The success of this program in creating an interdisciplinary research and educational effort is due to the cooperation of Rice and NASA in the development and implementation of the following goals:

1. The investigators, individually and in cooperating groups, should engage in original research that is relevant to the fundamental understanding of their scientific field and to specific materials problems that arise in the NASA programs.

2. The investigators and their students should try new ways to gain a broad understanding of solid materials. Each discipline should draw on the insights of every other discipline, where possible, and new instructional methods should be developed to prepare Ph.D. graduates whose competence transcends traditional disciplinary lines.

To achieve these goals, 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. Twenty faculty members were involved in the program as investigators. Also participating in the research efforts were 35 graduate students (8 foreign) and 6 postdoctoral fellows (4 foreign). Their research results are described in Section II. A total of 18 publications resulting from this work is given in Appendix I.

2. The third year of an interdisciplinary seminar program was completed.

3. The second year of the interdisciplinary course sequence in the physics of solids described in Status Report #17 was completed. This sequence is an important part of the program in solid materials and will be expanded in the future.

4. Increased emphasis is being placed on closer relations with investigators at other NASA laboratories. The intention of this program is to encourage research collaboration. Funds from the grant will be used to facilitate travel for these purposes.

The research reports given in Section II are presented in a form that has been evolving over the last several status reports. The research efforts have been grouped in five areas, and a single investigator from each area has prepared the progress report. It is our intention to make these reports useful summaries at an interdisciplinary level.

The weekly interdisciplinary seminar has become a useful and important part of the educational program. It is a major point at which interaction can occur between faculty, graduate students and postdoctoral fellows from the various disciplines. Some of the recent seminar topics were:

1. Fluctuations in Superconductors
2. Elastic-Wave Propagation in Anharmonic Media with Resonant Absorption and Dispersion
3. Radiation Hardening of Neutron-Irradiated Cu-Au Single Crystals
4. Phenomenological Theory of Magnetostriction in the Rare Earths
5. Work Hardening in Cu_3Au.

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

1. Electron Transport and Superconductivity (3)
2. Magnetism and Magnetic Resonance (8)

Several additional students and staff members audited these courses. This program has proven to be quite successful and will be continued as planned into the third year. A proposal to broaden the series to include a basic course in surface physics (e.g. "Surface Phenomena and Catalysis") is presently under discussion. A survey has also been made of advanced course offerings that treat solid-state topics (see Appendix II). These courses should be integrated more thoroughly into an organized materials program.

Efforts to establish significant contacts between Rice investigators and those with similar interests in NASA laboratories are continuing and will be expanded in the future. During this reporting period the Lewis Flight Propulsion Laboratory, Cleveland, was visited by Professors P. L. Donoho and R. B. McLellan, two staff members from Lewis were on campus to visit Professor J. L. Margrave, and the Manned Spacecraft Center, Houston, was visited by Professors H. C. Bourne, L. E. Davis, and H. E. Rorschach. Visits to other laboratories are being planned to identify mutual interests.

The interdisciplinary character of the work supported by this grant has always been an important guideline in the development of our program. For this reason, we were disturbed by a recent article in the May, 1969, issue of the Journal of Metals by Professor S. V. Radcliffe in which the impact of the IDL pro-programs was criticized. A reprint of our reply to this article, also published in the Journal of Metals, may be found in Appendix III. It gives some indication of the impact of the NASA IDL program at Rice.

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

II. Research Reports

A. Mechanical Properties and Defect Structure of Solids- N. Soga

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
N. Soga - Assistant Professor of Space Science

The research in this field at Rice University is centered about the studies of elastic and plastic phenomena which take place upon deformation of matter. Considerable insight into the internal structure of matter, both on the atomic and electronic scale, has been obtained through these investigations. Furthermore, clear explanations of various observations on the elastic and plastic behavior of materials will eventually lead to future development of new materials and the improvement of existing materials.

The theories concerning elasticity of solids have been extensively developed in the past 150 years. Besides their practical value in engineering, the elastic constants are of interest in solid state studies because of the insight they give into the binding forces of solids. There remains, however, a large number of problems. One of them is a theoretical treatment of the nonlinear response of elastic media now being studied by Professor J. D. Ingram and his students at Rice.

On the other hand, the theories concerning plasticity are less developed despite the great research effort aimed at understanding lattice imperfections, notably point defects and dislocations. Consequently, the progress in plasticity depends largely upon an empirical approach, in which the composition is systematically varied and the correlations with the resulting properties determined. Contributions made by Professor J. M. Roberts and his associates during this reporting period to a general understanding of work hardening phenomena are noteworthy in this respect. The details of their results will be described later.

A wide variety of experimental techniques is being employed to study the elasticity and plasticity of solids. They include special methods for microplasticity work, electron microscopy for slip line studies, ultrasonic interferometry for elastic constant measurements, and paraelastic resonance methods for the study of point imperfections. The latter, being used by Professor T. L. Estle and his students, are based on the principle that monochromatic phonons can produce intense electric dipole transitions in nonmetallic crystals with isolated point imperfections because of a strong coupling of most paraelectric imperfections to stresses. Currently, they are attempting to observe this phenomenon at a frequency of approximately nine GHz in a lithium-doped KCℓ crystal.

Another unique instrument at Rice is the one-dimensional nonlinear string, constructed by Professor J. D. Ingram and his students for studying one dimensional torsional waves. They have collected the experimental data photographically from this nonlinear string, analyzed the spectra and found good agreement with their theoretical predictions for the nonlinear response of one-dimensional elastic media to stress. Although the theoretical progress on computation for higher dimensional models has been slowed by the algebraic complexity of such theories, further experiments designed to extend the results to higher dimensions are under way.

As was mentioned earlier, a certain insight into the interatomic forces and electronic structure of transition metals and alloys can be obtained through the investigation of their elastic constants. Although this approach has been undertaken by various investigators in the past, little is known about the effect of the addition of another metal on the interatomic forces of the base metal. Both Professors F. R. Brotzen and N. Soga have been conducting research in this field, particularly on refractory metals alloyed with rhenium, because of the growing industrial concern with ductile refractory alloys. It has been well established that the addition of rhenium increases the ductility of certain base metals. Some progress has been made since the last report. Through further analysis of the experimental data on the pressure and temperature derivatives of the elastic constants of molybdenum-base rhenium alloys, Professor Soga has found an unusually large anharmonic contribution to the interatomic forces in molybdenum alloys with high rhenium content. This seems to indicate that any theoretical approach based on a central force model may not be adequate to interpret the interatomic forces of such alloys. In order to clarify this point, he is currently conducting measurements of the pressure derivatives of elastic constants at low temperatures where the anharmonicity is expected to be small.

After their success in a qualitative interpretation of the elastic constants of transition-metal alloys in terms of their electronic structure, Professor F. R. Brotzen and his students are now attempting to link changes in the elastic properties, as a result of alloying, with dislocation behavior and plastic flow in these materials. The experimental results on molybdenum-base rhenium alloys show that relatively small changes in elastic properties can affect plastic flow properties significantly. Furthermore, the increased tendency toward deformation by twinning can be correlated with certain trends in the elastic constants. Since it is possible to predict the elastic constants qualitatively on the basis of electronic structure, they believe that the plastic properties can also be interpreted in terms of the electronic structure of alloys. The determination of the anisotropic Hall coefficients for transition-metal alloys, which is now under way, is aimed at obtaining further information concerning the electronic configuration of these alloys.

Molybdenum-base rhenium alloys are also used by Professor J. M. Roberts and his students to study the ductile-to-brittle transition in refractory metals. As described in the previous progress report, they have found that the relaxed stress in tantalum and molybdenum and their alloys with rhenium is related to the structural stress and is highly temperature dependent, as is the structural stress. To clarify such a large temperature dependence, they approached the problem by defining the relaxed stress as the thermal component of the flow stress when the anelastic strain rate has become very small. They have found that the activation enthalpy for stress relaxation increases linearly with temperature as expected from a thermally activated process. Further observations showed that the activation enthalpy at zero effective stress remains constant for molybdenum and its alloy with rhenium, whereas that for tantalum-base rhenium alloys increases with rhenium content. A full interpretation of these results is under way.

Another project related to dislocation motion in metals and alloys is the study of the work hardening characteristics in ordered and disordered metals and alloys which is being carried out by Professor J. M. Roberts and his associates. During this reporting period, they have determined the unidirectional damping loops, the nonelastic strain recovery and the slip line characteristics of ordered and disordered Cu_3Au single crystals in order to test several theories concerning work hardening. Thus far, these experimental results do not seem to support any of the existing theories, including the recent one based on a large unidirectional friction drag on edge dislocation in ordered Cu_3Au, developed by Professor G. C. Schoeck while he was a visiting professor at Rice during the academic year 1968-69. Some of the most important findings are as follows: The only significant difference between ordered and disordered crystals from the microplasticity viewpoint is the annealing effect upon the damping loop in ordered Cu_3Au crystals. The nonelastic strain recovery is proportional to the prestrain for both ordered and disordered Cu_3Au, and their magnitudes are similar. The lengths of the slip lines for ordered Cu_3Au are much larger than had been expected from the existing theories. They also found evidence of cross-slip in disordered crystal and some indication for cross-slip in the screw dislocation traces in the ordered crystals. The details of the experimental results are now being prepared for publication.

Finally, in order to analyze a large amount of data on internal friction and plastic deformation obtained in the past few years at Rice from work supported by the NASA Materials Grant, Professor J. M. Roberts is now exploring the relaxation loss mechanism and hysteretic loss mechanism associated with dislocation intersections by going through an intensive survey of recent publications. As a consequence, he now postulates that the temperature dependence of the stress to produce a vanishingly low strain rate for molybdenum may be attributed to dislocations overcoming tetragonal impurity distortions. Also, recognizing the importance of evaluating the attack frequency of a dislocation against a potential barrier, he is examining several different potential functions.

B. Electrical and Optical Properties - F. K. Tittel

Staff: L. E. Davis - Associate 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

The program of research on electrical and optical properties is concerned with investigating the electronic structure of solids and their interaction with electromagnetic waves over a wide range of frequencies. Special emphasis is given to the feasibility of developing new electronic devices. Studies in the following four principal areas have been performed.

(1) Microwave Properties

The behavior of ferrites in non-reciprocal microwave devices is being investigated by Professor L. E. Davis. Although microwave ferrite circulators have been known since the 1950's only in recent years have efforts been made to put this work on a surer theoretical footing, and the H-plane waveguide device is now fairly well understood (see earlier reports). During the period of the present report this work has concentrated on the E-plane waveguide circulator. There is no theory in the literature for this device because the usual simplifying assumptions are not valid with this structure. However, a solution is now becoming more urgent as the practical advantages of the structure are realized. The general theory of wave propagation in gyrotropic media has been reviewed in detail; a few contributions have been made (as yet unpublished) and the various advantages of the earlier analyses in some special cases have been brought out explicitly for the first time. The particular ferrite/waveguide structure of interest in the circulator problem can now be handled in a self-consistent way. An "equivalent resonator" approach to the E-plane waveguide junction necessitated an analysis of resonant cavities with an evanescent section, and also a general theory for matching lossless 2-port networks. This work has been presented in two papers.

The objective of the work of Professor T. L. Estle has been to obtain detailed atomic-scale descriptions of isolated point imperfections in nonmetallic crystals by microwave spectroscopic studies of their low energy states. Paraelectric resonance and electron paramagnetic resonance are used to study systems with permanent electric and magnetic dipoles respectively. (See earlier reports) Such detailed knowledge of the defect properties of solids will lead to future advances in solid state materials technology and the many activities dependent on obtaining still better materials. There is a strong coupling of most paraelectric imperfections to stresses. Hence transitions can be excited by lattice vibrations. This process is known as paraelastic resonance if artificially generated monochromatic phonons are employed. An attempt is being made to observe this phenomenon at around 9 GHz.

Professor T. A. Rabson and his students are investigating Gunn effect devices. Their research efforts are specifically directed toward the theoretical and experimental investigation of the effects of device geometry on Gunn effect instabilities through the analysis and fabrication of multidimensional devices and toward the study of voltage frequency tuning. Conduction anisotropy studies in bulk GaAs devices will also be carried out. Some multidimensional devices with annular geometries were fabricated with photofabrication techniques having various sizes and several radii ratios for comparison purposes. A sophisticated capacitive microprobe was designed and fabricated for potential and electric field probing. Numerical analysis of the conduction equations as applied to the Gunn effect devices with generalized geometries, field distributions, band structures and circuit conditions is being performed with a Burroughs 5500 digital computer.

(2) Optical Properties

The properties and applications of new optical devices based on the nonlinear characteristics of certain optical crystals is being studied by Professor F. K. Tittel and his students. A specific goal is to develop a continuously tunable CW parametric oscillator at optical frequencies, which would benefit such diverse technical disciplines as optical communications, spectroscopy, laser interferometry and nonlinear optics. Central to the operation of a parametric oscillator is the fact that a sufficiently strong pumping field can drive signal and idler fields through interaction in a nonlinear crystal whose temperature and orientation satisfy the momentum matching condition at three frequencies. A versatile opto-electronics facility has been built, which has so far been successfully used to study frequency doubling and continuously tunable parametric noise involving $LiNbO_3$ and $Ba_2NaNb_5O_{15}$ crystals and visible or infrared CW coherent light sources. A major effort has gone into the careful analysis and testing of the individual optical components comprising the entire system. In particular, mode selection and mode locking techniques were developed for a CW argon laser. The second harmonic output from a number of crystals from three different commercial sources was also investigated in order to characterize an optimum parametric oscillator configuration.

(3) Gamma-Ray Properties

Professor G. T. Trammell and his group have developed a comprehensive theory for the interaction of Mössbauer gamma rays with matter. The basic theoretical development is discussed in previous reports. This work is being extended to apply the theory to the analysis of experiments, and to investigate possible new uses for these unique rays. The theory was applied to the results of experiments designed to test the time reversal invariance of nuclear interactions utilizing Mössbauer gamma rays. A second application of the theory consisted of explaining the dispersion term which was observed by Sauer, Mathias, and Mössbauer in the absorption spectrum of the 6.25 kev Ta^{181} resonance. This is the sharpest of all Mossbauer lines yet studied and has great potentialities for solid state studies.

The fundamental limitations on the possibility of forming an image of a molecule in which the individual atoms are resolved has been examined theoretically. It has been shown that any attempt to form an image of an atom in a molecule will, with a high probability, rupture or alter its bonds to its neighbors, which will in turn rearrange their positions and couplings during the process of observation.

C. Magnetism and Superconductivity - G. T. Trammell

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 magnetic interaction is one of the three long-range interactions (together with the electric and gravitational interactions) existing in physical systems. It is this, along with the fact that all spinning objects have magnetic moments and give rise to magnetic fields, which accounts for the pervasive importance of magnetic studies in all the branches of physics ranging from study of the structure and dynamical properties of the elementary particles to that of the stars and galaxies.

The magnetism related research sponsored by NASA at Rice includes the studies in rare earth magnetism by Professors P. L. Donoho and G. T. Trammell, the studies of point imperfections in crystals by means of paramagnetic (and paraelectric) resonance absorption techniques by Professor T. L. Estle, the studies of the magnetic properties of superconductors by Professor H. E. Rorschach, and the rock-magnetism studies of Professor H. C. Clark for use in the investigations of the paleomagnetic state of the earth and, possibly, other planets.

(1) Rare Earth Magnetism

In recent years technological advances in metallurgy have made rather pure rare earth samples available and relatively inexpensive. As a consequence of this, and of their interesting and useful magnetic properties, a large fraction of current magnetism research involves these materials.

The rich variety of the magnetic behavior of rare earth materials is due in large part to the peculiar importance of the crystalline fields in determining the properties of these substances. The basic theoretical discussion of the effect of strong crystalline fields on the spontaneous magnetization of concentrated rare-earth materials stemmed from research carried out under this grant a few years ago. The novel spin wave excitations to be expected in these "induced moment" systems and the theoretical prediction of a new type of magnetic ordering phenomenon (heat magnetization) were discussed in subsequent publications. This field of induced moment systems--in which the ordered magnetic moment arises via a "boot-strap" process when the interatomic exchange forces are sufficiently large to overcome the disordering effect of the crystalline field--is currently in a stage of rapid experimental and theoretical development in a number of laboratories, as well as being a subject of continuing theoretical development here.

In this research of Professor G. T. Trammell and his coworkers the significance and relevance of the crystal field supermultiplets or bands in determining the properties of certain cubic rare-earth compounds was emphasized. The existence and importance of this supermultiplet phenomenon is, however, not restricted to rare-earth ions in fields of high symmetry, and

Professor G. T. Trammell in collaboration with Professor Rudolf Mössbauer and Mr. E. Seidel of the Technische Hochschule, München, is now involved in extending the theory so as to explain the peculiarities (related to the existence of bands or super-multiplets) of the crystal field levels of wide variety of rare-earth compounds of low point symmetry.

The "crystal field energy" of a rare-earth ion refers to the coulomb interaction of the aspherical charge distribution of the 4f shell electrons of the rare-earth ion with that of the other ions and electrons in the crystal. The strength of the intraatomic spin orbit energy results in the symmetry axis of the 4f charge distribution being tightly coupled to the spin axis of the ion and hence gives rise to a large anisotropy in the dependence of the energy on the spin, or magnetization, direction.

By way of contrast the magnetic anisotropy energy of the 3d (iron group) metals is several orders of magnitude smaller than for the rare earths because there is only a very weak coupling between the spin direction and the symmetry axes of the 3d charge distributions when the ion is in a crystal.

An important consequence of the large magnetic anisotropy energy of the rare earths is that they also exhibit very large magnetoelastic effects. For example, the magnetostriction coefficients of the 3d metals are only of the order of a few times 10^{-5}, whereas for Dysprosium the coefficient is 7.5×10^{-3}, and it is of the same order of magnitude for other rare earths. In order to understand the magnetic properties of a metal such as Dysprosium it is essential to take proper account of its enormous magnetoelastic coefficient. This had not been done in previous theories. Professor P. L. Donoho and his co-workers have now developed a theory of the magnetic properties of Dysprosium, including the theory of its magnetoelastic waves, which accounts in a satisfactory way for these properties. In addition they have begun experimental studies of the magnetostrictive properties of Dysprosium single crystals firmly bonded to a nonmagnetic solid aiming towards the construction of a highly efficient microwave frequency transducer. They have observed that the bonding has a strong effect on determining the critical field for the helimagnetism to ferromagnetism transition, and that the magnetostriction is markedly reduced by the clamping effect of the bonded material. These effects were expected. They believe, however, that the clamping effect will not markedly reduce the transducer efficiency when it is driven at the frequency of the magnetoelastic resonance which they found and reported earlier. Construction of a microwave transducer is being continued.

In addition to the work on Dysprosium, Professor P. L. Donoho and his students have also completed a study on magnetic resonance absorption in single Holmium crystals. Because of relatively poor crystal quality, no true resonance was found; but a strong field-dependent absorption attributable to magnetoresistance effects was observed.

(2) Point Imperfections in Nonmetallic Crystals

A free electron, being a spinning body, possesses a magnetic moment which is a very accurately known fraction $g\beta$ of its spin angular momentum. In an applied magnetic field H it will then precess with an angular frequency $\omega_B = g\beta H$ which may be measured from the frequency at which maximum absorption of energy is obtained when the electron is also subject to a small sinusoidally oscillating magnetic field. If the electron is not free but is centered at a certain site in a crystal, then its precession frequency will be changed from the value $g\beta H$ because of various additional torques to which it will be subjected. These torques come from the magnetic moments of the nuclei in its vicinity, the magnetic moment of its own orbital motion, the electrostatic torques acting on its orbital motion, and other effects. The measurement of the resonant frequency shift of electrons in crystals as a function of the applied field direction reveals remarkably detailed information concerning the environment of the spinning electron, and has, indeed, been the chief source of our knowledge of the strengths of the crystalline fields, the spreading out of the electron wave function in molecules and crystals, the electron-phonon interactions, and numerous other physical effects.

In addition to their paramagnetic resonance studies Professor T. L. Estle and his co-workers are constructing apparatus for resonance studies of paraelectric imperfections in nonmetallic crystals. In this relatively new field one determines the influence of the environment in determining the oscillation frequencies of an impurity which possesses a permanent electric moment. In analogy to the paramagnetic technique this may be done by studying the absorption spectrum when the sample is subjected to an oscillating electric field; however there are also strong couplings of paraelectric imperfections to lattice strains, and Professor T. L. Estle and co-workers are preparing to detect these characteristic paraelectric vibrations by phonon resonance absorption. In their initial experiment a 9GHz ultrasonic pulse will be generated in a lithium doped KCℓ crystal and the echoes studied as a function of a variable applied electric field.

(3) Magnetic Properties of Superconductors

A superconductor makes a transition to the normal conducting state when it is placed in a magnetic field $H > H_c$, the critical field. For some very pure (type I) superconductors, however, the field H can then be diminished to a value $H_s < H_c$ before the transition back to the superconducting state is made. In the region $H_s < H < H_c$ the sample is said to be "supercooled" or "undermagnetized," it being in this region in a metastable state having a larger free energy than that of the superconducting state. The metastability arises because of the existence of a "nucleation barrier" inhibiting the initiation of supercurrents.

Professor H. E. Rorschach and his students have begun an experimental study of high purity, zone refined, single crystals of molybdenum in order to isolate the factors determining the region of metastability and the values of H_c, H_s, and T_c for these "ideal" samples. At the present time they have completed a systematic study of the effect of annealing on the supercooling properties. The annealing was carried out in high vacuum at temperatures of 1100°C and 1200°C for a range of annealing times up to 180 hours. For a particular sample studied, H_s/H_c (for temperatures near T_c) was found to remain equal to one (no detectable supercooling) up to annealing times of about 100 hours, then to fall rapidly to about 0.2 at 140 hours, followed by a slower decrease to 0.18 ± 0.05 at 180 hours. According to a theory of De Gennes and Saint James, H_s cannot be lower than $H_{c_3} = 2.4\ KH_c$, where the "Landau-Ginsberg Kappa factor" is the ratio of two characteristic lengths of a superconductor, since at H_{c_3} there is no barrier to the nucleation of surface supercurrents. The change in H_s which was observed upon annealing was presumably due to the change in the defect structure of the crystal, but an electron microscopic surface replica study showed that even the unannealed sample had a very low density of defects (less than $10^8/cm^2$) and after annealing this number was too small to be observed. The measurements showing the remarkable dependence of H_s on a small number of defects in these highly purified single crystals cannot be reasonably accounted for by the De Gennes mechanism, and constitute a challenging problem for theoretical explanation.

(4) Magnetic Properties of Rock

One of the most valuable properties of a rock is the remanent magnetization its ferromagnetic minerals acquire as it cools, since under favorable circumstances it can serve as a record of the paleomagnetic field. The weak original magnetism, however, is often masked by magnetizing influences in its later history, and Professor H. C. Clark has been pursuing research directed towards determining the nature of these "spurious" magnetizations.

Work has been completed on a suite of volcanic rock in the Big Bend region of Texas. The secondary magnetism caused by lightning, was successfully removed and the weak original magnetism recovered. The resulting paleomagnetic pole information indicates that the distance between North America and Europe has increased since the formation of these volcanic rocks some 30 million years ago.

Work is continuing on rocks in the Llano area of Texas, which at 1 billion years are some of the oldest in this country. In addition, experiments to determine the relation between the cooling history and a reliable record of the paleomagnetic field are underway.

D. Thermodynamics and Solid Surfaces - T. W. Leland

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

(1) Studies Involving Bulk Solid Properties

Studies carried out by the investigators listed above include research on thermodynamic behavior of bulk solids and also investigations studying the properties of the solid surface and its interactions both with the underlying bulk region and with various fluids contacting the surface. Research centered mainly on bulk solid properties will be discussed first.

a. Application of Mössbauer Spectroscopy to the Study of the Thermodynamic Properties of Alloys

The thermodynamic studies of the bulk solids are making use of some new tools and procedures which are providing powerful new methods for studying thermodynamic behavior. M. L. Rudee and R. B. McLellan are utilizing some unique applications of Mössbauer spectroscopy in this manner. The temperature dependence of the Mössbauer resonance is being used to gain information about the lattice dynamics of binary alloys containing iron in dilute concentrations. The position and strength of the Mössbauer resonance are related to the vibrational behavior of the iron in the lattice.

Studies of a range of known compositions of iron in platinum are planned. From these studies it is possible to obtain the vibrational contribution to the excess entropy of mixing. These results, when combined with those of other investigators on the total excess entropy, make possible an unusually complete thermodynamic study of the solid solution. This is particularly important because it makes possible direct experimental measurements of thermodynamic properties of iron in solutions at extremely low concentrations to obtain information on the limiting behavior of the solution. Work during the past period on this project has been spent on developing a cryostat to maintain the sample at accurate low temperatures while providing gamma ray transparent windows to observe the spectrum. Preliminary measurements have been made and a number of modifications are currently underway to improve their precision.

b. Interstitial Solid Solutions

Professor R. B. McLellan is also studying both thermodynamic and kinetic properties of interstitial solute atoms in various solid solutions. The objective is to determine the energy and entropy of the solute and, in the same solution, to calculate the mobility of the solute atoms to furnish information on their diffusional characteristics. During the past period a number of accomplishments have been made:

1. The equilibrium between CH_4-H_2 mixtures and carbon in alpha iron has been measured at 735°C to accompany previous data measured at 800°C.

2. An X-ray investigation of the dilation of the palladium lattice with dissolved carbon has been made. This yields information on the local strains around the solute atoms which will be correlated with previous thermodynamic measurements on the Pd-C system.
3. Previous theoretical models for interstitial solid solutions have been used to calculate the mobility of carbon atoms in gamma iron using absolute rate theory.
4. A first-order statistical mechanical model for interstitial solid solutions has been set up. It has been shown that this theoretical model is consistent with both the diffusion of carbon in gamma iron and its equilibrium properties
5. The thermodynamic properties of carbon atoms in solid gold, copper, and silver have been measured by solubility measurements over a wide temperature range.
6. It has been shown that the entropy and energy of monovacancies in metal lattices can be calculated from models based on linear elasticity assumptions.

Plans for the continuation of these studies include measurements of the equilibrium solubilities of CH_4-H_2-C in iron at additional temperatures; diffusivity measurements of carbon in delta iron and chromium; studies of the Ni-Cu-C system using vapor transport methods; continuation of current X-ray and electron diffraction studies of the order-disorder reaction in solutions of 3% silicon in iron; continuation of recently started mass-spectrometer Knudsen cell studies of the thermodynamics of silver solutions; and extension of the successful statistical models developed for binary solutions to ternary solid solutions.

c. <u>Properties of Materials at High Temperatures and Pressures</u>

Professor J. L. Margrave and his co-workers have been continuing their studies of the behavior of various inorganic materials at high temperatures and/or high pressures with the objective of establishing thermodynamic stabilities and molecular parameters.

An ingenious technique called levitation calorimetry is being used for the determination of thermodynamic properties at very high temperatures. This technique studies materials for which a small droplet or particle can be suspended in a magnetic field and brought to high temperatures by RF induction heating. This eliminates the problems of structural failure or contamination inherent in selecting a container for the material at these extreme conditions. This method is being applied to the study of high temperature thermodynamic properties of the high melting metals like molybdenum, tantulum and tungsten.

X-ray diffraction methods are being used to study high pressure phases and a new apparatus has been designed to perform X-ray diffraction studies using polychromatic methods on samples at high pressures and high temperatures. Tests are being planned to establish the reliability of high pressure polychromatic X-ray methods. If these are successful, future plans are to use these methods to supplement several studies on metal oxides at high pressures.

Recent developments in laser technology are being applied to study the evaporation induced by rapid absorption of high energy fluxes. Plans are to study high molecular weight clusters produced by this technique. During the past reporting period the laser apparatus has been used successfully in polymer evaporation studies and is currently being improved. The species evaporated or sublimed by the laser beam are identified with a time-resolved mass spectrometer.

(2) Studies Based on Surface Properties of Solids

The many diverse physical and chemical phenomena which result from the unique properties of a solid surface, the characterization and description of solid surfaces, and the relationship between bulk properties and surface properties all constitute a vast and complex branch of the physics of solid materials. Considerable progress in this area has been made during the past reporting period and is summarized below.

a. Adsorption of Gases and Liquids on Solid Surfaces

Professor R. Kobayashi has been continuing his studies of solid surfaces using some new developments in gas chromatography. With these developments it is possible not only to measure directly the quantity of material adsorbed but also it is possible for the first time to measure directly the volume of the adsorbed layer. The quantity adsorbed and its equilibrium partition between gas and solid phases can be determined by passing the adsorbing gas through a chromatographic column packed with the granular solid. The gas is allowed to flow until steady state conditions result. Then a radioactive isotope pulse of the same gas is injected into the stream and the retention time for the pulse is measured by observing its emergence into a radiation detector at the end of the column. The equilibrium adsorption can be calculated from this quantity.

The size of the adsorbed layer may be determined by injecting a sequence of pulses of monatomic gases with decreasing molecular sizes into the flowing stream of the adsorbate gas. For example, the sequence, Krypton, Argon, Neon, Helium produce a sequence of slightly different retention times. By plotting these times one can extrapolate to find the retention time of a hypothetical ideal gas with zero molecular volume and zero intermolecular attraction. From this extrapolated time Professor R. Kobayashi has shown that one can calculate the volume of the adsorbed layer.

A study has been underway to measure adsorption isotherms of methane on uniform finely ground glass beads and to measure the volume of the adsorbed phase. The results show that this volume appears to be very nearly constant, independent of temperature and coverage. This volume is useful in revealing the structure and nature of the adsorbed layer on the solid. Heats and entropies of adsorption have been determined from the complete adsorption isotherms and give some information on the heterogeneity of the surface. Future plans call for the extension of this technique to study physical adsorption on other surfaces.

b. Surface Interactions on Ferrite Catalysts

Professor Hightower and his colleagues are attempting to establish a correlation between solid state properties of spinel-type materials and surface interactions with molecules from the gas phase during catalytic reactions.

The importance of the surface of solid materials in determining their catalytic activity cannot be overemphasized. While it may not be so difficult to characterize many of their bulk properties, techniques which focus only on the surface layer of solids are extremely complicated from an experimental standpoint and are in general difficult to interpret theoretically. Furthermore, most of the environmental conditions necessary to perform these experiments are frequently far removed from reality in requiring ultrahigh vacuum and/or cryogenic temperatures.

The philosophy behind the current investigations is to use a heterogeneous catalytic reaction as a probe of the surface condition of several spinel-type ferrites and to attempt to correlate the observed activity and/or selectivity with bulk solid properties. The initial reaction chosen was the commercially important oxidative dehydrogenation of n-butenes to butadiene. Other possible reactions with this system include olefin isomerization, polymerization, partial oxidation, and total oxidation to carbon dioxide and water. Magnesium ferrite, $MgFe_2O_4$, was the first material studied, and the results of some mechanistic studies involving use of both deuterium and C-14 tracers were reported earlier. An irreversible decline in both the catalytic activity and selectivity was observed. X-ray analyses of the solid showed significant changes which varied systematically with catalyst aging.

Mössbauer adsorption spectra have now been carried out on these same catalyst samples. The structural changes are due to the disappearance of an α-Fe_2O_3 impurity phase, present in the fresh starting material, which parallels the activity decline. It thus appears that the catalytic activity may be due not to the spinel structure per se, but to impurity centers or imperfections in the crystal structure that anneal under more severe reaction conditions.

Additional work is currently underway with other ferrite and non-ferrite spinels to determine if this behavior is general. Future plans are to broaden the scope of these experiments to include other spinel-type oxide materials both with and without iron as the major metal.

c. Surface States in Metal Oxides and Their Effect on Catalytic Behavior

Professor T. W. Leland and co-workers have completed a study of the effect of surface ultraviolet irradiation in altering the catalytic activity of MgO for the H_2-D_2 exchange using a high pressure mercury lamp ultra violet source. A new series of studies irradiating MgO and also ZnO is now underway using an improved tungsten filament discharge uv source which has a much more uniform source intensity distribution over a wide frequency range.

The role of adsorbed water in controlling the effect of the irradiation has been studied thoroughly. It was found that MgO caralysts largely freed of chemisorbed water by strong preheating in vacuum are insensitive to ultraviolet radiation. Catalysts which retained some chemisorbed water after moderate preheating show a large enhancement in catalytic activity following ultraviolet irradiation of the surface. It has also been shown that the effect of the ultraviolet irradiation is definitely not one of merely removing water from the surface.

These studies, along with subsequent experiments using controlled ultraviolet irradiation frequencies and tracer studies with the mass spectrometer have shown that hydrogen from the adsorbed water on the surface definitely participates in the H_2-D_2 exchange reaction. The mechanism for the UV induced reaction on the water-containing surface is definitely different from that on the more water-free surface without irradiation. Mechanisms for the two surfaces have been proposed in a recent paper.

The effect of varying the ultraviolet frequency has also been studied. The ultraviolet enhancement in activity of a partially dehydrated MgO surface can be entirely removed by gentle annealing. This allows the enhancement produced by a specific frequency to be studied, thermally erased, and then a different frequency applied to the same surface for study.

The activity of magnesium oxide powder for the hydrogen-deuterium exchange reaction was studied in this manner as a function of surface irradiation with controlled frequencies of ultraviolet radiation from a monochromator. A succession of ultraviolet energies from 3 to 7 ev was applied to the surface and the relative enhancement of the first-order rate constant produced at saturation for each frequency was plotted against the ultraviolet energy. The relative enhancement of the rate constant shows well-defined peaks at 5.7, 4.9, and 4.0 ev. By comparison with work of other investigators on optical absorption, photoconductivity, and electron paramagnetic resonance studies on MgO irradiated with ultraviolet, it is possible to state quantitatively the energy of the electronic transitions affecting the catalyst, and in some cases, to identify the physical nature of the excitation. This technique constitutes a type of reaction rate spectroscopy and is now being applied in studying electronic factors in other insulator and semiconductor catalytic surfaces.

A series of reactions such as the H_2-D_2 exchange, CO oxidation, methanol oxidation and decomposition are being planned for study on MgO and ZnO catalysts. The frequency dependence of the radiation enhanced reaction is to be measured to attempt to explain the reaction in terms of published electronic state data.

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 substrates. 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 (permalloy) 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 addition, the same motion generated by slow rising pulses or low-frequency continuous-wave excitation has been investigated. The rate of change of the field is too low to produce the gyromagnetically-induced motion of the fast-rising pulses, described above. After extensive experimental work using a new high-resolution Bitter technique as well as Kerr magneto-optic techniques and electronic pickup signals, a new mechanism for wall motion has been discovered. Very rapid displacements of the wall take place at certain critical fields. The nature of the motion is such that only a gyromagnetic origin seems plausible. However, the necessary step field applied to the wall appears to originate in an instability in the magnetization in the domains on each side of the wall. A sudden change in the magnetization in the domains applies the demagnetizing field to the wall and causes a motion consistent with experimental observations. The key to this instability probably rests in the theory of the small magnetization variations in nominal single domains often referred to as ripple theory. Although other mechanisms may be partially responsible for this "creep" of domain walls, the mechanism described appears to be the fundamental one.

In Materials Science, Professor M. L. Rudee and his students have been studying the relation of magnetic properties to structural aspects of permalloy 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. This is the magnetostrictive constraint theory. 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 verified that the constraint mechanism accounts for part of the anisotropy, although there is a small difference in magnitude between the experiments and the theoretical predictions. From these same experiments, it also appears that the remainder of the anisotropy originates in the directional ordering of pairs of iron atoms in the solid solution. This latter mechanism is the same one that is believed to produce the magnetic annealing affects observed in bulk samples of permalloy.

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, and for the most part its dispersion, are largely reversible. From measurements on a large number of films, an empirical relation between the magnitude of the anisotropy and its dispersion has been observed that is independent of composition. This relationship is not in agreement with the often quoted results of the ripple theory, the fundamental theory relating the properties of magnetic films to their structure. However, the technique used here to determine the anisotropy is sensitive to contributions to the anisotropy of all wavelengths, while the approximations used in the ripple theory restrict its validity to the short wave length components. In order to pursue this line of research further, a device is under construction that will measure the dispersion from small regions so that the contribution of the various wavelengths can be separated.

Appendix I

Publications during the Period of this Report

A. Mechanical Properties and Defect Structure of Solids

1. N. Soga

"Elastic Properties of CaO under Pressure and Temperature."
J. Geophys. Res. 73, 5385 (1968).

2. N. Soga
"Elastic Constants of Polycrystalline BeO as a Function of Pressure and Temperature."
J. Am. Ceram. Soc. 53, 246 (1969).

B. Electrical and Optical Properties

1. F. M. Stuber and L. E. Davis
"Resonance Frequency Behavior of a Cavity with an Evanescent Section."
Accepted for publication in Electronics Letters (October 1969).

2. T. K. Gaylord, P. L. Shah and T. A. Rabson
"Gunn Effect Bibliography."
IEEE Trans. on Electron Devices, Vol. ED-15, No. 10, pp. 777-788, October 1968.

3. T. K. Gaylord, P. L. Shah and T. A. Rabson
"Gunn Effect Bibliography Supplement."
IEEE Trans. on Electron Devices, Vol. ED-16, No. 5, pp. 490-494, May 1969.

4. T. K. Gaylord and T. A. Rabson
"A Method for Estimating the Location of Energy Minima near the Brillouin Zone Boundary and its Application to Gallium Arsenide."
Accepted for publication in Physics Letters.

5. J. P. Hannon and G. T. Trammell
"Mössbauer Gamma Ray Optics II."
Accepted for publication in the Physical Review.

6. G. T. Trammell with J. P. Hannon
"Interference of Electronic and Nuclear Absorption for Mössbauer Gamma Rays."
Phys. Rev. 180, 337 (1969).

C. Magnetism and Superconductivity

1. M. W. Gilliland, H. C. Clark, and J. F. Sutter
"Paleomagnetism of the Buck Hill Volcanic Series, Big Bend, Texas."
Transactions of the American Geophysical Union, Vol. 50, No. 4, April 1969.

2. G. T. Trammell and E. R. Seidel
"Simple Crystal Field Effects on Rare Earth Ions."
Accepted for publication in the Physical Review.

D. Thermodynamics and Solid Surfaces

1. P. J. 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 the J. Inorg. Nucl. Chem.

2. D. W. Muenow, J. W. Hastie, R. Hauge, R. Bautista, and J. L. Margrave
"Vaporization, Thermodynamics and Structures of Species in the Tellurium-Oxygen System."
Accepted for publication in the Trans. Faraday Soc.

3. R. H. Siller and R. B. McLellan
"The Dilation of the Palladium Lattice with Dissolved Carbon."
Accepted for publication in the J. Less-Common Metals.

4. R. B. McLellan
"The Elastic Calculation of the Entropy and Energy of Monovacancies in Metals."
Trans. AIME, Vol. 245, p. 379 (1969).

5. W. W. Dunn and R. B. McLellan
"First-Order Mixing Statistics of Interstitial Solid Solutions."
Accepted for publication in the J. Phys. Chem. Solids.

6. R. B. McLellan
"The Solubility of Carbon in Solid Copper, Gold, and Silver."
Scripta Met. 3, 389 (1969).

7. R. H. Siller and R. B. McLellan
"The Variation with Composition of the Diffusivity of Carbon in Austenite."
Trans. AIME 245, 697 (1969).

E. Thin Magnetic Films

1. H. C. Bourne, Jr., T. Kusuda, and C. H. Lin
   "A Study of Low-Frequency Creep in Bloch-Wall Permalloy Films."
   Accepted for publication in IEEE Trans. on Magnetics.

2. K. R. Carson, F. A. Wierum, and M. L. Rudee
   "Departure from Free Molecular Flow During the Boat Evaporation of Permalloy."
   Accepted for publication in J. Vac. Sci. and Technol.

3. M. L. Rudee, S. J. Horowitz, and K. R. Carson
   "The Composition Dependence of the Magnetization Induced Uniaxial Anisotropy in Both Normal and Unconstrained Ni-Fe Thin Films."
   Accepted for publication in J. Appl. Phys.

Appendix II

Solid State Courses

1. Basic Sequence:

Chem., E.E., M.E., Physics	563	Introduction to the Solid State
	564	Electron Transport and Superconductivity
	565	Dielectric and Optical Properties of Matter
	566	Imperfections and Mechanical Properties
	567	Magnetism and Magnetic Resonance

2. Related Courses:

Chemistry	610a	High Temperature Chemistry
"	660a	X-ray Crystal Structure Analysis
Chem. E.	560a,b	Heterogeneous Equilibrium and the Phase Rule
"	594a,b	Polymer Science
	690a,b	Kinetics and Catalysis
E. E.	661	Semiconductor Electronics
"	662	Ferromagnetic Theory and Devices
"	666	Quantum Electronics
"	669	Direct-Energy Conversion Devices
M. E.	536	Introduction to X-ray Diffraction and Electron Microscopy
"	541	Physical Metallurgy
"	542	Nonmetallic Materials
"	628	Theoretical Plasticity
"	629	Applied Plasticity
"	634	Thermodynamics of Alloys
"	635	Transformations in Alloys
"	636	Diffraction in Nonideal Crystals
"	644	Lattice-Imperfection Theory
"	645	Mechanical Metallurgy
Geology	440a	Introduction to Geophysics
"	582b	Meteoritics
Physics	520a,b	Principles of Quantum Mechanics
"	600a,b	Special Topics in Solid-State Physics
"	630a	Advanced Quantum Mechanics

Letters to the Editor

Graduate Education

I wish to call to your attention some serious errors in the article by S. Victor Radcliffe on "Two Decades of Change in Graduate Education in Metallurgy/Materials—A Perspective", which appears in the May 1969 issue of the Journal of Metals. That is, figures shown for Penn State are in gross error. On July 1, 1967 a Materials Science Department was formed, comprising the sections of Ceramic Science, Fuel Science, Metallurgy and Solid State Science. The department administers graduate degree programs in these four areas, and undergraduate programs in the first three areas. At present we have a total of 163 graduate students and 122 undergraduate students.

Specific corrections which should be made in the above article are:

Table I should read:

Number of Doctorates Awarded		
1954	1956	1968
11	8	17

Table II should read:

Number of Doctorates 1967	1968	Mean	Masters	Bachelors	Faculty
16	17	17	16	33	35

The figures in Table IV, which lists the number of advanced degrees awarded in the state of Pennsylvania in 1968, should also be changed.

Previously, Penn State was not even listed in Table II. On the basis of the above data, Penn State will rank second over-all in the table and also second in the areas of Ph.D.'s awarded and faculty members.

P. L. Walker, Jr., Head
Materials Science Department
Pennsylvania State University

Interdisciplinary Laboratories

The May 1969 issue of the Journal of Metals contained an article by Professor S. V. Radcliffe entitled "Two Decades of Change in Graduate Education in Metallurgy/Materials—A Perspective." In it, Professor Radcliffe offered an analysis of the impact of the federally supported interdisciplinary laboratories (IDL) on graduate education in metallurgy and materials engineering. The article contains a most valuable collection of data on the production of graduate degrees in the engineering disciplines concerned with materials. Mainly through the emphasis given to certain aspects of the subject, the article suggests findings which, in our opinion, could be misleading and require clarification.

From the very name of the IDLs, it is clear that one of the principal premises for their creation was their interdisciplinary character. Professor Radcliffe acknowledges this by the statement (page 30) that only 20% of the faculty members supported by these grants were metallurgists, while physicists comprised the largest group (40%). Yet, in his presentation, Professor Radcliffe measures the production of graduate degrees by including only those from engineering departments of metallurgy and materials, as defined by the U. S. Office of Education, while omitting completely all graduates in other disciplines. If we use the degree of support as an estimate of the number of students, then we would conclude that only one fifth of the relevant students have been included, and perhaps less. Moreover, the output of some schools which have important programs in materials, such as Brown, Chicago, Harvard, Maryland, North Carolina and Rice, were completely excluded because the designation of their degrees did not qualify for inclusion, according to the definitions used in the available data. The figures used by Professor Radcliffe were undoubtedly the only ones readily available, but it appears unwise to make the analysis of a small part the basis for a critique of the whole.

The history of the NASA supported IDL at Rice University offers a good example of an analysis of the effectiveness of these grants in graduate education in the field of materials taken in its broadest sense. The number of Ph.D. degrees in materials awarded by science and engineering departments during the ten-year period since the inception of the NASA IDL at Rice is summarized below:

1960	4
1961	2
1962	7
1963	8
1964	8
1965	12
1966	13
1967	15
1968	12
1969	10
Total	91

This increase is significantly more than the rise in number of degrees conferred in metallurgy and ceramics alone, as presented in Professor Radcliffe's article, Fig. 2. If we adopt a starting number of four graduates for the first year, then the total number of degree awards, 91, corresponds to an average yearly growth of 17.5%, well in excess of the average of 12% in the overall growth rate of engineering doctorates as given in Fig. 4 of Professor Radcliffe's article. (An average growth rate of 12% would have resulted in a total production of 70 degrees during the ten-year period.) It seems likely to us that other universities may have had a similar experience. The significance of these figures for such a relatively small university as Rice suggests that Professor Radcliffe's conclusions could be profoundly modified by the inclusion of similar data from other universities.

The distribution of support from the IDL grants among several disciplines was a conscious effort to alter not only the size but also the character of graduate programs in materials. Clearly, it is much more difficult to measure the quality of an educational effort than its output in number of graduates, but it is certainly no less important. Professor Radcliffe recognizes the innovative aspects of the IDLs, but discusses this important matter only briefly. His emphasis on some of the quantitative aspects of the IDLS, we believe, fails to place the beneficial nature of their interdisciplinary structure in a balanced perspective. The structure of the IDL at Rice has strongly encouraged both a broadening of the instruction and a relaxation of departmental boundaries and thereby has enriched the background of our graduates.

In conclusion, we believe that the true importance of the IDL programs in materials can only be assessed if the full impact of these programs is considered for all of the university disciplines that are involved. Any other analysis will omit the most important feature of these programs—their interdisciplinary character.

Franz R. Brotzen,
Professor of Materials Science;
H. E. Rorschach,
Professor of Physics;
M. L. Rudee,
Associate Professor of Materials Science;
Rice University
Houston, Texas

Dr. Radcliffe Replies

I am writing in response to the two recent letters to the Journal of Metals from Professor F. R. Brotzen et al. of Rice University and

(Continued on next page)

Appendix IV

Financial Report
NASA Grant NsG6

	Report of Expenditures			
	For the Period 1/1/69 to 6/30/69		For the Period 5/1/69 to 6/30/69	
Salaries				
Professional	$ 43,914.47		$ 763,650.90	
Students	12,477.47		446,392.10	
		$ 56,391.94		$ 1,210,043.00
Overhead				
At 50% of salaries included in the first $1,150,000 expended			$ 235,429.10	
At 25% of Direct Cost not to exceed $120,000 of next $600,000 expended			120,000.00	
At 20% of Direct Costs		17,617.12	155,731.28	
				511,160.38
Expendable supplies and Materials	$ 25,735.05		$ 482,705.00	
Minor Equipment	5,958.83		158,811.88	
		$ 31,693.88		$ 641,516.88
Major Equipment		-0-		321,652.30
Commitments Outstanding				
Materials and Supplies	$ 13,293.63			
Equipment	19,604.48			
Overhead for Commitments	6,579.63	39,477.74		39,477.74
Totals	$ 145,180.68			$ 2,723,850.30

Major Equipment: None