Facility

WILLIAM MARSH RICE UNIVERSITY

HOUSTON, TEXAS

Semiannual Status Report #12

On

NASA RESEARCH GRANT NO. NsG-6-59

Covering

Research on the Physics of Solid Materials

For the Period

1 November 1964 through 30 April 1965

Under the Direction

Of

Franz R. Brotzen

During the six years that this grant has been active at the Rice University, the funds have been utilized for two primary goals:

(1) To develop a strong graduate education program in the science and engineering of materials.

(2) To stimulate both fundamental and applied research on solid materials.

At the end of the present academic year 5 masters degrees and 10 doctors degrees will be awarded to students that have been active in research sponsored by this grant. A total of 44 graduate students are involved in 35 projects under the direction of 18 faculty members. In addition, 9 post-doctoral fellows are employed on various projects sponsored by this grant, and a few particularly well qualified undergraduates are employed as technicians during the summer months. Competition for these latter positions is quite intense, and it is hoped that this experience will encourage some of these particularly able students to continue in the fields of materials research.

This grant is supporting research in six different departments. There is a significant amount of both formal and informal inter-disciplinary cooperation. Among the more recent cooperative ventures of a formal nature are the cooperative development of advanced crystal growing facilities to serve both the materials science and the solid state physics groups and the establishment of a joint graduate training program in solid state electronics and materials science. In addition numerous small pieces of equipment are shared and various joint seminars are often scheduled.

A brief description of the progress on various projects is included as a part of this report. The publications resulting from this research are mentioned in Appendix I.

I. Solid State Physics

A. Paramagnetic Spin-Lattice Interactions

Dr. P. L. Donoho, Department of Physics

Most of the effort has been concentrated on finishing up the relaxation measurements in ruby, which have gone on for some time. A paper on this work was presented at the Berkeley American Physical Society meeting in December, and the results of the work are being prepared for publication. Work has been started on the measurement of much shorter relaxation times, down to a few microseconds, but only preliminary results are available so far.

B. Phonon-Phonon Scattering

Dr. P. L. Donoho, Department of Physics

This work has been concluded with a successful development of the theory to give excellent agreement with experimental results. The work is being prepared for publication.

C. Ferromagnetic Spin-Lattice Interactions in Rare Earth Thin Films

Dr. P. L. Donoho, Department of Physics

This work is most promising. In examining the magnetostrictive production of microwave phonons in ferromagnetic and antiferromagnetic Dysprosium and Holmium a very strong effect was found whose details are presently under intensive investigation. The spin-lattice interaction for rare-earth metals is much stronger than for iron-group metals, leading to interesting practical applications, such as the possibility of microwave low-loss delay lines, acoustic amplifiers, etc.

D. Superconductor Tunneling

Dr. P. L. Donoho, Department of Physics

The first successful Josephson tunneling junctions have been made and attempts to detect the interaction of the Josephson current with microwave phonons are underway. This work should lead to a better understanding of electron-phonon interactions in superconductors.

E. Laser Research

Dr. T. A. Rabson, Department of Electrical Engineering

Two projects are currently being carried out; one involves the measurement of the polarization of the light output of light-pumped solid-state lasers, and the other is concerned with the use of a high energy, ruby laser to vaporize sources for a mass spectrometer.

As has been reported previously, the light output of neodymium-doped glass lasers has been observed to vary from spike to spike. Measurements have been made of the polarization for

several different pumping energies, and a theory is being developed in an attempt to explain the effect.

A high energy, ruby laser has been built and operated, but as yet its energy output has not been measured. Techniques are being developed to use this laser to vaporize small amounts of material that will be introduced into a mass spectrometer in order to make an analysis.

It is felt that the laser polarization experiment will aid in giving a better understanding of the laser process and will perhaps yield some information concerning the electric fields in glass. It is hoped that the second project will lead to a method of studying the surface composition of materials such as semiconductors about which little is known at present.

F. Superconductivity of Niobium
Dr. W. V. Houston, Department of Physics

The work reported here is a general study of the behavior of superconducting materials, with particular reference to the time variation of the various phenomena. This involves such matters as the motion of the normal-to-superconducting boundary. Such properties are of crucial importance in considering the possibilities of superconducting DC generators.

There are presently five investigations under way:

1. Measurements were made of the electromotive forces along a superconducting wire carrying a large alternating or a changing direct current. It was shown that a fairly good quantitative description of the effect can be given in terms of a model, previously suggested by Bean of the Bell Telephone Laboratories, which relates the current density at a point in the wire to the magnetic field at that point.

2. The force on a superconducting tin disc was investigated when the disc moves in a concentrated magnetic field. The magnetic field is so designed as to penetrate the disc in a small spot of material which remains normal as the disc is cooled. The results show that an attempt to move this spot meets with a large force which is a function of both the displacement and the velocity. This work was reported in a preliminary way at the February meeting of the American Physical Society in Norman, Oklahoma.

3. An apparatus is being constructed for a different approach to the same problem as the above, No. 2. There will be a narrow strip of superconducting material on the surface of a plastic disc and the change in energy of the disc will be measured as the superconducting material passes through a magnetic field on the one hand, a concentrated beam of light on the other, or both of them together. No results are yet available.

4. The way in which superconductivity is destroyed by magnetic field in the case of tin is being studied. Thus far the apparatus has been built and its constants are being determined in order that changes in times of the order of 1/10 of a millisecond may be observed.

5. Construction of and preliminary tests on an apparatus have been undertaken to determine with high precision the amount of flux retained in a superconducting specimen when the superconductivity is destroyed by an external magnetic field. It is expected that the apparatus will be used to study various kinds of superconductors in fields as high as 4,000 gauss.

G. Mechanics of Magnetic Ordering (Particularly Rare Earth Metals and Compounds)
Dr. G. T. Trammell, Department of Physics

Recent work reveals that the usually assumed RKKY interaction form is simply wrong for the rare earths: not only are there non-isotropic exchange contributions of the order of the isotropic terms, but the radial dependence of the isotropic term itself differs significantly from the RKKY expression.

A variety of unusual magnetic effects which stem from the peculiar nature of the rare earth compounds have been investigated theoretically; they have been reported on at various scientific meetings, and the results will be submitted for publication by the summer's end.

H. The Magnetic Properties of Insulating Crystals
Dr. H. E. Rorschach, Department of Physics

Previous experiments on the nuclear spin-lattice relaxation times in insulating crystals containing rare-earth ions have been extended to CaF_2 containing Neodymium. The relaxation time has been measured as a function of temperature and orientation, and a new effect observed. The relaxation time becomes strongly orientation-dependent at temperatures near 100°K, and it is believed that this dependence is due to a new interaction between the electronic spins and the nuclear spins.

This interaction could prove to be an important consideration in the evaluation of such substances for use as laser crystals or for the polarization of nuclei by the "solid effect". This work is also being extended to include measurements of the magnetic susceptibility as a function of crystal orientation in the anomalous region.

I. Ferromagnetic Properties of Thin Films
Dr. H. C. Bourne, Jr., Department of Electrical Engineering

A study of the loss mechanisms in ferromagnetic thin films as a function of a variety of deposition parameters, temperature, and drive will yield general information on significant properties of ferromagnetic materials.

Design and construction of the experimental equipment has progressed satisfactorily. Several cube coil assemblies have been built. The substrate heater, mask, and shutter system have been designed so that the evaporating system is operative. The external coils to provide appropriate fields during evaporation to fix the film easy axis have been developed and installed. The general theories involved in vacuum evaporation of thin films as applied to this system plus various means of monitoring evaporation rates have been studied and applied. A hysteresis loop tracer for obtaining thin film loops over a frequency range of 100 cps to 25,000 cps and a film thickness variation of 50 A to 5000 A has been built and used. A more elegant version has been designed and is being fabricated which extends the range and will also incorporate the possibility of wide temperature variations. Switching apparatus to measure the film characteristics in the low-to-medium-speed range has been developed and used to measure film characteristics. The apparatus involved 10 ampere, 2 μsecond circuitry. The apparatus is currently being designed and built to include the low-damping, high-speed coherent rotation region.

Data from the versatile BH loop tracer provides a means of studying these loss mechanisms in a quantitative manner. The relatively large drives of the high-speed switching experiments will permit the formulation and study of more sophisticated theoretical models for the dynamic behavior of the magnetic moments of ferromagnetic materials.

J. Radiant Energy Conversion
Dr. G. C. Jain, Department of Electrical Engineering

This is a project begun in the later part of the reporting period. The aim of this project is to study the quantum efficiency of incident radiant photons in Ge p-n junctions. Equipment for the preparation of the junctions is being set up.

K. Ferroelectric Energy Conversion
Dr. G. C. Jain, Department of Electrical Engineering

Just like the previous project, this one was started in the later portion of the reporting period. The aim of this investigation is to dope Barium Titanate with suitable impurities so that it can be used efficiently to convert heat into electrical energy directly.

II. Physical Metallurgy

A. Dislocation Contrast and Dislocations in a Semi-Infinite Region

Dr. W. B. Pfeiffer, Department of Mechanical Engineering

The investigator has returned to Germany. The manuscripts covering his most recent work are presumably being prepared for publication.

B. The Influence of Solute Atom Additions and Temperature Upon the Damping and Yield Phenomena in Magnesium Single Crystals

Dr. J. M. Roberts, Department of Mechanical Engineering

The results of this study earlier reported have been collected in the form of a Ph.D. dissertation. The dissertation will be the basis for three articles to be submitted for publication in the near future.

C. Microcreep of Molybdenum Crystals

Dr. J. M. Roberts, Department of Mechanical Engineering

This phase of the project is being completed under the direction of Dr. F. R. Brotzen, since Dr. Roberts has been on leave for one year. The following is a summary of this work:

Molybdenum single crystals 1/8 inch in diameter were tested in a special creep machine using a very sensitive capacitance-type extensometer. Microcreep of the crystals was studied at stresses below half the macroscopic yield stress in the temperature range 200°-300° K. at resolved shear strains below 5%.

The creep following the addition of a stress increment was found to have two parts. In the initial period, the creep rate decreased rapidly, but approached a constant value in from one to ten minutes. Study was concentrated on that latter portion of the creep, i.e., constant creep rates in the range 10^{-9} to 10^{-6} sec.$^{-1}$. The effects of temperature, effective stress, and prior strain were studied. The effective stress is the externally applied stress less the internal back-stress in the material. It is this net stress acting on dislocations which causes them to move. The internal stress was measured by finding the stress at which the onset of backward creep could be detected. This appears to be the first time that the internal stress has been measured directly in a body-centered cubic metal.

The constant creep rate which was approached following the initial period obeyed an equation of the form

$$\dot{\gamma} = A \sinh (v\tau^*/kT),$$

as has been predicted for creep at very low effective stresses. The activation volume v was in the range 15-40 b^3, decreasing with strain and decreasing at lower temperature. The parameter A of the above equation contains the density of activable segments of dislocation. The increase of A with strain was found to be proportional to the increase of dislocation density as re-

ported in the literature. From the temperature dependence of the parameter A, the activation energy for the constant rate microcreep was found to lie in the range of 0.1 ev. Results indicate that the high values of over 1.0 ev. obtained by other investigators for deformation of b.c.c. metals arises from neglect of the change of the internal stress with temperature.

The internal stress was found to rise strongly with a decrease of temperature with the same temperature dependence as that of the macroscopic flow stress. Extrapolation of the data obtained indicates that the internal stress should tend to zero at about 360° K which is the region above which the macroscopic yield stress of molybdenum has been found to become temperature independent. The internal stress did not appear to be an innate property of the b.c.c. lattice but developed as the consequence of small amounts of strain. Some indication has been found that the internal stress decreases over a period after the material has been unloaded or as the material is being allowed to warm-up following low temperature deformation.

No definite model for the creep process or for the recovery of the internal stress has yet been worked out. However, it is thought that cross-slip of screw dislocations plays an important role. It has been concluded that the strong temperature dependence of the flow stress of molybdenum at low temperatures is due to a very high rate of work-hardening which strongly increases the internal stress during low temperature strains of 10^{-3} or less.

D. Phonon-Dislocation Interactions

Drs. P. L. Donoho, Department of Physics, J. M. Roberts and F. R. Brotzen, Department of Mechanical Engineering

The observations made with LiF crystals have been reported earlier. A manuscript was forwarded to NASA and a short paper was submitted to and accepted by the journal physica status solidi.

E. Ultrasonic Attenuation of LiF crystals Between 2° and 300° K

Drs. M. Yabe and J. M. Roberts, Department of Mechanical Engineering

Construction of the equipment is almost finished. The internal-friction measurement of gamma-irradiated LiF crystals at low temperatures will start soon after a malfunctioning sampling oscilloscope is repaired.

An improvement was made in the cryogenic system, including the liquid-helium cryostat for the irradiation experiment and the temperature-measuring system. Moreover, the performance of the electronic system for measuring the internal friction was improved to obtain more reproducible and more accurate measurements. Preparation of specimens with the high precision essentially for the experiment has been successfully accomplished.

An experimental study is in progress for an acoustical composite system which includes a quartz transducer, a very thin visco-elastic adhesive layer, and a large sample. This study will contribute to the knowledge about the configuration of defects in LiF produced

at low temperatures as well as about their migration, interaction and transformation. Also, some dynamical properties of dislocation in LiF at low temperatures will be investigated.

F. Electrical Resistivity of Deformed Molybdenum Single Crystals
Dr. F. R. Brotzen, Department of Mechanical Engineering

Previous results indicated an increase in resistivity which was linear with strain for a deformation temperature of 195° K. The linear relationship has been verified at 195° K to approximately 6% strain. At 273° K the resistivity versus strain curve was found to have a small negative curvature.

The relative magnitude of the resistivity due to point defects and dislocations was evaluated by annealing at 473° K. For deformation at 195° K both the resistivity increase due to point defects and that due to dislocation was found to be linear with strain, the contribution due to point defects being approximately 20% of that due to dislocations. When deformed at 273° K the resistivity increase due to point defects was linear with strain and the resistivity increase due to dislocations had a small negative curvature. At 8% strain the increase in resistivity due to point defects was found to be approximately 20% of the increase due to dislocations.

G. Observation of Dislocations in Molybdenum
Dr. F. R. Brotzen, Department of Mechanical Engineering

Molybdenum single crystals are being strained in direct shear to known strains at various temperatures. Dislocation density measurements are being made on these crystals through transmission electron-microscopy and electrochemical etch pitting. During the current research period, techniques and apparatus for straining 1/8 inch diameter molybdenum crystals in direct shear have been built and an apparatus for removing 0.010 in. thick slices from these crystals by electric spark machining has been developed. A reliable technique for producing electron microscopy specimens from these disks has been established. A technique for etch pitting the disks for observation of dislocation densities has also been developed. Testing of specimens, and dislocation density measurement has begun.

H. Mechanical Properties of Molybdenum Single Crystals
Dr. F. R. Brotzen, Department of Mechanical Engineering

The electron beam zone refiner is being redesigned in order to produce purer single crystals than are grown at present. Evaluation of the effect of small amounts of impurities on the stress-strain relationship and activation volume in shear and tension will begin after the modifications of the zone refiner are complete.

I. Study of Shear Fracture of Elastic Materials
Drs. J. Cl. De Bremaecker and L. Mansinha, Department of Geology

Many materials exhibit transverse anisotropy i.e. the elastic

properties are identical in all directions in a plane normal to a symmetry axis. The elastic properties in the direction of the symmetry axis are different from those normal to it. Engineering materials like rolled sheet metal or plate glass, as well as floating ice sheets and hexagonal crystals possess such transverse anisotropy. A formal solution of a special problem of fracture propagation in a transverse isotropic medium has been developed. Numerical computation of the solution is in progress at present.

Work on fracture propagation along bimaterial interface has been completed and is in the process of publication.

J. X-Ray and Resistivity Studies of Transformations in Ti-V Alloys
Dr. F. R. Brotzen, Department of Mechanical Engineering

Work and results of this project were reported earlier. A manuscript is presently being prepared for publication.

K. Short-Range-Order and Electrical Resistivity in FCC Alloys
Dr. M. L. Rudee, Department of Mechanical Engineering

The effect of short-range-order (SRO) on the electrical resistivity in alloys that have unfilled d-bands has been treated theoretically. To provide experimental data to test these calculations, the resistivity, and the degree of SRO, will be measured in Pd-Au mono-crystals. Different degrees of SRO will be produced by various quenching treatments and the Cowley SRO parameters will be measured by analyzing the diffuse scattering of x-rays. The electrical resistivity of the sample will also be measured. A doubly bent crystal monochrometer and a single crystal orienter have been installed on the x-ray diffractometer, and the alignment has been completed. Computer programs have been written for the analysis of the data. In addition, an improved expression relating the Cowley SRO parameters to the various atom-pair-energies has been developed. The experimental phase of this research is now beginning.

An additional closely related topic is being investigated simultaneously. In certain FCC alloys it has been observed that the electrical resistivity decreases during the early stages of plastic deformation. The effect has been attributed to either the destruction of SRO, or changes in the number of carriers produced by the generation of dislocations. A series of experiments are in progress to differentiate between these two explanations.

These topics are of importance to the advancement of the understanding of materials because probably all alloys are non-random to some extent. The effect of the deviation from randomness by SRO on electron transport has been treated theoretically only superficially and no thorough experiments have been reported.

L. Kinetics of Short-Range Ordering in Cu-Au
Dr. F. R. Brotzen, Department of Mechanical Engineering

By measuring the resonance frequency in an electro-mechanical circuit, similar to the one described by Folweiler and Brotzen (Acta Met. 7, 715 (1959)), very small changes in the elastic modulus are observed. The kinetics of the ordering process at constant temperature in quenched Cu-Au specimens can be observed by this method. The elastic modulus rises rapidly at the beginning of the ordering treatment. At low temperatures it approaches a constant value, but develops a maximum at higher temperatures.

The kinetics are checked by electrical resistivity measurements. Data are still incomplete and do not yet permit an unequivocal interpretation.

M. Inter-Relation of the Electronic Structure and the Nature of Crystalline Defects in Semi-Conductors
Dr. M. L. Rudee, Department of Mechanical Engineering

One of the active areas of research in materials science is the determination of the relationship between the nature of crystalline defects and the electronic structure of the material. Most of this research has been performed on pure metals and alloys. Unfortunately in these systems the electronic structure is only sparsely documented.

Similar research in semiconductors is being initiated not only because the results in semiconductors will be of inherent interest, but also because the electronic strucutre in these systems is well known.

Recent results in another laboratory indicate that the plastic properties of Germanium are strongly dependent on whether the material is n or p type, and whether it is in the temperature range of intrinsic or extrinsic conductivity. Research is being initiated to study the effect of the electronic state of the material on the nature and properties of the crystalline defects. Specifically, it is contemplated to investigate the stacking-fault energy and dislocation mobility in Si as a function of doping and temperature.

This program has been dormant during the present reporting period but work should be re-initiated during the next reporting period.

III. Chemistry of Solids

A. Monte Carlo Calculations for Lattice Systems

Dr. Z. W. Salsburg, Department of Chemistry

The program for investigating order-disorder transitions reported earlier has been reprogramed for the CDC 6600 computer at the Lawrence Radiation Laboratory in Livermore, California, and is currently in operation. However, several months of computer usage will be necessary before any specific results can be obtained.

B. Limiting Properties of Hard Sphere Solids and Harmonic Crystals

Dr. Z. W. Salsburg, Department of Chemistry

An interest in the effect of anharmonic forces on the thermodynamic properties of crystalline solids at high temperature and pressures has initiated the following program:

A technique has been developed for obtaining a systematic series of approximations to the free energy of a system at high temperatures and pressures. This procedure starts with the Einstein single-particle approximation (or its analogous single-particle cell theory for rigid spheres) and then corrects this for successive two particle, three particle, etc., correlations in a lattice of monatomic molecules. The general technique has been applied to a system of two-dimensional rigid disks in a triangular lattice, and an article outlining this procedure has been accepted for publication in the August issue of the Journal of Chemical Physics. Work is currently in progress on obtaining the free energy of three dimensional spheres in the hexagonal and face-centered lattices and on a two dimensional harmonic crystal.

It should be emphasized that this technique is valid only at high temperatures and pressures. It is in this region, however, that the following properties will be explored:

1. The free energy function of a perfect crystal.
2. The free energy of formation of mono-and di-vacancies and their equilibrium concentration.
3. The effect of anharmonic forces on the elastic constants of solids.
4. The radial distribution function in high density solids.
5. The Debye-Waller factor at high temperatures and pressures.

C. Thermal Emittance Measurements of Nickel Single Crystals as a Function of Oxide Thickness

Dr. W. W. Akers, Department of Chemical Engineering

Additional studies have been conducted to determine the effect of oxidation on the total hemispherical thermal emittance of the

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C. Thermal Emittance Measurements of Nickel Single Crystals as a Function of Oxide Thickness

Dr. W. W. Akers, Department of Chemical Engineering

Additional studies have been conducted to determine the effect of oxidation on the total hemispherical thermal emittance of the

(100), (110), and (111) crystal faces of nickel. Most of the single crystal samples needed to complete the work have been prepared.

Thermal emittance determinations on the (110) crystal face have been completed. Some of the (100) crystals have also been studied. Initial data indicated a broad minimum in the "emittance vs. temperature curve" for the single crystals. Additional studies showed the minimum to be due to heat conduction losses to the sample holder. This resulted from the fact that the single crystals were approximately 20 times thicker than the polycrystalline nickel foils previously used. This problem was solved by spot welding heat sinks (thin polycrystalline foils) on each end of the nickel crystal sample.

At the present time, insufficient data are available to speculate whether a difference will be seen in the emittance curves for the different crystal faces. A difference, as expected, has been observed in the oxidation rate of the (110) crystal as compared to the (100) crystal. The (110) crystal was observed to oxidize more rapidly, since it is less-closely packed than the (100) crystal.

Color photomicrographs (1000X) have been taken of the various stages of oxidation of the (110) and (100) crystals. The pictures clearly indicate the nuclei formation of the oxide on the nickel crystal surface.

D. Kinetics of Oxidation of Nickel
Dr. W. W. Akers, Department of Chemical Engineering

Work has not yet been completed on the measurements of the rate of oxidation of nickel in the "medium" film region. This work provides a bridge between the very thin film measurements done previously in this laboratory and the thick film parabolic region that has been reported in the literature. The work substantiates proposed theories in regard to the change from logarithmic rate to a quartic rate, to a cubic rate, and, finally, to a parabolic rate as the thickness of the oxide film increases. The results are in excellent agreement with the prior work.

E. High-Temperature Interactions Between Gases and Condensed Phases
Dr. J. L. Margrave, Department of Chemistry

1. Vapor Pressure Measurements

Studies of kinetic and thermodynamic phenomena characteristic of gas-solid interactions have been continued. The Ainsworth semi-micro recording balance has been utilized for total weight-loss measurements (Langmuir and Knudsen) on CdF_2, CoF_2, ScF_3, LaF_3, $KMnF_3$, and $KCoF_3$. Mass spectrometric studies of FeF_2 have established the vapor species as $FeF_2(g)$. In reducing environments one forms mono-fluorides with binding energies about 8-10% less than predicted on the basis of average bond energies for the difluorides. In addition, Knudsen sublimation and vapor pressure measurements have been made on a

variety of organic molecules of different symmetries.

$NbSe_2$ is reasonably stable at temperatures above 1000°C after losing excess selenium and reaching an equilibrium stoichiometry. Weigth-loss and mass-spectormetric studies are in progress.

2. Kinetic Studies

The ion source of a Bendix Model 14 time-of-flight mass spectrometer is being modified to permit studies of the interaction of a molecular beam and a heated metal surface. A component has been designed and is being built that will allow a metal ribbon (or wire) to be mounted several millimeters away from the ionizing electron beam, perpendicular to a molecular beam and with the capability of being translated out of the molecular beam. The primary experimental variables are: (1) molecular beam on or off (with a shutter), (2) electron beam on or off, (3) ribbon surface in or out of molecular beam, and (4) the temperature of the metal ribbon. The manipulation of the variables allows one to distinguish between the mass spectra due to (1) background or residual gas, (2) the reactant molecular beam, (3) the reflected but unreacted beam, (4) a surface ionized product, and (5) a neutral product evaporating from the ribbon.

As a first experiment a study will probably be undertaken of the kinetics of the surface dissociation and ionization that occurs when alkali halide beams impinge on various polycrystalline refractory metal surfaces.

The behavior of materials at extreme conditions (high temperature, low pressure, corrosive environments, etc.) must be known in order to provide a basis for extension of theoretical principles and extrapolation of engineering design correlations. The studies underway in this project provide useful information about thermodynamic, geometrical and statistical factors important in gas-condensed phase interactions under reducing, neutral and fluorine-rich atmospheres.

F. Crystal Structure of Complex Molecules
Dr. R. L. Sass, Department of Chemistry

Work done during the last six months is a continuation of the program in the general area of the determination of crystal structures of complex ionic compounds. The major fraction of this work has been on the structures of certain carbanions. We have previously reported on the structures of ammonium tricyanomethide and pyridinium dicyanomethylide in which the carbanion was found to be significantly nonplanar. We have since completed the structure of potassium paranitrophenyldicyanomethide. Our results show the carbanion group to be coplanar, as might be expected from the pressure of the nitro group in the para position. In order to further investigate the dependence of the geometry of the car-

banion on substituent groups we are presently engaged in the determination of the structures of ammonium trinitromethide and several conjugated systems.

The structure of paradiazoniosulfonate has also been determined. The dimensions of this zwitterion are comparable with those of known normal diazonium salts. Finally the structure of cis-2-butylene episulfone has been completed. An abnormal feature of this structure is the rather long observed C_2-C_3 bond distance of 1.59 A indicating a considerable amount of strain in the three-numbered ring.

G. Radiation Effects on Metallic Films and Surfaces of Solids
Dr. T. W. Leland, Department of Chemical Engineering

The apparatus reported as under construction in the last progress report has now been completed. It consists of a very sensitive quartz bourdon tube with an optical system to measure the deflection occurring with the reaction rates over single crystal surfaces. A separate apparatus to measure conductivity and Seebeck EMF for the single crystal in the same environment is under construction.

The study of radiation-induced perturbations of the Fermi Level described in the last report is continuing. A new power supply and more intense ultra violet source has been selected for the Beckman spectrophotometer in our Department. This will allow the instrument to be used as a monochromator for ultraviolet radiations of catalyst samples at a precise frequency.

Measurements of the catalytic activity of chemically doped MgO for the H_2 - D_2 exchange reaction is continuing as described in the last progress report. The analytical technique has been improved.

H. The Nature of Gaseous-Solid Interfaces
Dr. T. W. Leland, Department of Chemical Engineering

Work on the Nature of Gaseous-Solid Interfaces is continuing A series of measurements of absorption equilbra of methane-propane mixtures on charcoal surfaces has been completed. These data are being analyzed by means of the two dimensional equation of state developed by the project.

I. Study of Hydrates
Dr. R. Kobayashi, Department of Chemical Engineering

Statistical mechanics of spherical and non-spherical molecules was used in the study of hydrates of binary gas mixtures of such molecules. Using the Kihara potential for non-spherical molecules the hydrate theory has been applied to study the hydrate

formation conditions of nitrogen, ethane, and propane and ternary mixtures of these molecules with methane and water. The hydrate formation conditions are in reasonable, if not exact agreement, with experimental measurements. The hydrate phase composition for the methane nitrogen-water system showed substantial discrepancies between the experimental and theoretical results, even though the predicted hydrate formation conditions are in reasonable agreement with the experimental values. Until the experimental determination of the hydrate phase compositions is improved considerably, it will not be possible to resolve this disagreement.

Construction of an apparatus for the direct determination of hydration numbers of gas hydrates is proceeding. The apparatus when completed, will be first applied to show experimentally that the hydrate numbers along the univariant hydrate-liquid-water-gas changes progressively towards its asymptotic value at high pressures.

J. Adsorption of Gases on Solids at Elevated Pressures
Dr. R. Kobayashi, Department of Chemical Engineering

Gas-solid chromatography has been previously developed in these laboratories to permit the measurement of the adsorption of gases at infinite dilutions at high pressures. The general theory for van der Waals type adsorption was also derived and a limited application of the theory was carried out for mixtures of methane and propane on silica gel. Recent improvements in the experimental techniques and interpretation of the data have permitted:

1. Determination of pure component adsorption data at high pressures by a perturbation technique.

2. Determination of adsorbed volumes by a perturbation technique.

3. Removal of the sample size effects by using radioactively traced hydrocarbons to effect the perturbation.

4. The initiation of a program to obtain component and total adsorption data over a rather wide range of pressure and temperatures for the methane-propane system.

K. Study of Phase Transitions in the Methane - Propane-n-Decane System
Dr. R. Kobayashi, Department of Chemical Engineering

Following a check of a previous experimental determination of the solid-liquid-vapor locus for the methane-n-decane system, data are being obtained on the location of the solid-liquid-vapor locus for the methane-propane-n-decane system. To date, the runs of a 3 mole per cent propane - 97 mole per cent methane mixture indicate that a pronounced displacement of the solid-liquid-gas locus as the pressure of the system is increased occurs. The extent of the displacement is related to the increase solubility of propane in the liquid phase with increased pressure and decreased temperature.

Date: 8 June 1965

Signed: Franz R. Brotzen

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APPENDIX I

PUBLICATIONS DURING THE PERIOD OF THIS REPORT

Y. Kitano, F. Specht, and G. T. Trammel
"Dynamical Properties of Some Rare-Earth-Intermetallic Compounds"
Proceedings of the International Conference on Magnetism,
September 1964, Nottingham, England.

R. K. Watts
"Spin-Lattice Relaxation in Ruby"
(Paper Presented), Bull. Am. Phys. Soc., 9, 739 (1964)

M. P. Maley and P. L. Donoho
"Magnetostrictive Generation of Microwave Ultrasonics in Thin Films of Dysprosium"
(Paper Presented), Bull. Am. Phys. Soc., 10, 472 (1965)

F. H. Stillinger, Z. W. Salsburg, and R. L. Kornegay,
"Rigid Disks at High Density",
Accepted by Journal of Chem. Phys.

D. Lewis, M. Frisch, and J. L. Margrave
"Heats of Combustion of Some Pyrolytic Graphites",
Accepted by Carbon

R. H. Bautista and J. L. Margrave,
"Microbalance Studies of SrF_2 and BaF_2"
Accepted by Jnl. Phys. Chem.

R. Loehman, R. Kent, and J. L. Margrave,
"Vaporization of $SrCl_2$",
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G. C. Wetsel, Jr. and P. L. Donoho,
"Ultrasonic Paramagnetic-Resonance Absorption by Uranium Ions in Calcium Fluoride",
Submitted to Phys. Rev.

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"Tensile Fracture Along a Bimaterial Interface",
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L. Mansinha,
"The Moving Griffith Crack of Unvarying Shape",
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"Radioactive Doping of Cadmium Sulfide Films and Its Effects on Chemisorption"
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