WILLIAM MARSH RICE UNIVERSITY

HOUSTON, TEXAS

Semiannual Status Report #14

On

NASA RESEARCH GRANT NsG-6-59

Covering

Research on the Physics of Solid Materials

For the Period

1 November 1965 through 30 April 1966

Under the Direction

Of

Franz R. Brotzen

During the past years the NASA Materials Grant NsG-6-59 covering research on the Physics of Solid Materials has provided the principal stimulus for materials research at the Rice University. As a consequence of this grant, the number of Rice staff members concerned with instruction and research in the sciences and engineering of solid materials has increased continually. At the present time, the number of projects carried out under the sponsorship of this grant is 35. These projects are under the direction of 18 faculty members. A total of 35 graduate students are engaged in research fully or partly supported by this grant. There are presently also 4 post-doctoral fellows who derive their support from this grant. It should be noted that the personnel listed here represents only a portion of the total personnel at Rice engaged in materials research. No doubt, many projects that are not sponsored by this grant were stimulated by its presence.

The interdisciplinary nature of this grant, which has been pointed out in several earlier reports, has also produced benefits to the Rice University as a whole. The grant has served as a model for other programs of multidisciplinary nature at Rice. For example, it would hardly have been possible to establish the present interdepartmental program in applied mathematics and systems theory without the model of the interdisciplinary materials program sponsored by this grant. The University is presently actively looking for several new, young faculty members in the area of materials science. In this search emphasis is placed on the ability of these new faculty members to work closely with colleagues in different departments.

As in the past, an effort is made to classify, for the purpose of

this report, the projects sponsored by this grant according to three categories. The first of the three categories deals with "Solid-State Physics." It covers primarily the magnetic and electric aspects of materials research. The second category, denoted by "Physical Metallurgy," centers about work on metallic materials. The third category, "Chemistry of Solids," is concerned primarily with chemical reactions and thermodynamics involving solid substances. It should be noted that the three categories do not reflect departmental or other organizational divisions.

I. Solid-State Physics

A. Spin-Lattice Interactions in Paramagnetic Crystals

Dr. P. L. Donoho, Department of Physics

Objectives:

To understand the interactions between the magnetic moment of an ion in an insulating lattice and the vibrational modes of the lattice.

Report:

Most of the work has been theoretical, since the most important problem uncovered by the previous work of this group is the enormous discrepancy between theoretical and experimental values for the relaxation times of certain rare-earth ions in CaF_2. A new physical model involving ionic tunneling has been proposed to explain this discrepancy.

Experiments designed to test the tunneling model mentioned above are underway. By looking at ESR signals when a dc electric field is applied to the sample it will be possible to determine whether tunneling of interstitial ions is taking place.

B. Microwave studies of Single-Crystal and Thin-Film Ferromagnetic Rare-Earth Metals.

Dr. P. L. Donoho, Department of Physics

Objectives:

To understand the basic spin-lattice interaction in rare-earth metals, and to study the possibility of using the very large magnetostriction observed in these metals to develop a very efficient microwave ultrasonic generator and detector.

Report:

Preliminary measurements on the generation of microwave ultrasonic waves through magnetostriction have been completed, and they are summarized in the paper listed at the end of this report. Initial measurements of microwave power absorption in single crystals of dysprosium have led to the observation of magnetic-field-dependent absorption, of a type not previously reported, which is probably due to magnetostrictive losses.

More thorough investigations of microwave ultrasonic generation will be carried out. Better control of film preparation is now possible, so that results should be reproducible. The effect will also be studied with thin single-crystal platelets. An attempt will be made to correlate results with the present theory of magnetic properties of the rare earths.

C. Effect of Phonons on Josephson Tunneling Currents in Superconductors
Dr. P. L. Donoho, Department of Physics

Objectives:

To determine the role played by phonons, if any, in the various effects associated with superconducting tunneling junctions.

Report:

Experimental difficulties have proved insurmountable thus far, and the abandonment of the project is being contemplated. Certainly the goals must be changed. Josephson junctions have been produced in this group, but no success has been achieved in producing such junctions on an ultrasonic transducer.

The same experiment is being tried at audio frequency rather than microwave frequency because the transducer problem is much simpler.

D. Polarization Study of Stimulated Emission of Lasers
Dr. T. A. Rabson, Department of Electrical Engineering

Objectives:

To investigate the factors which determine the polarization of the light coming from lasers and the relations between modes of oscillation and the output wave form.

Report:

During the study of magnetic effects in a Nd^{3+} doped $CaWO_4$ laser, magnetic pole pieces with a maximum field intensity of about 30 KG have been mounted; matched laser pumping configurations have been constructed and are being used.

Future plans include research on the use of a microwave receiver to study the Zeeman effect for Nd^{3+} doped $CaWO_4$ lasers, the study of holography and wave front reconstruction, as well as light modulation and detection techniques.

E. The Time Development of the Meissner Effect and the Factors Influencing Trapped Flux
W. V. Houston, Department of Physics

Objectives:

To study the time dependence of magnetic field penetration.

Report:

The oscillograms obtained to represent the flux penetration into an

elliptical superconductor have defied an analysis precise enough to yield significant information about the onset of the Meissner effect. Attention has been turned to a high precision and detailed study of trapped flux, which has identified three distinguishable sources of trapping. There are microscopic surface irregularities which give a distinctive pattern of flux trapping. There are internal trapping centers distributed through the volume of the material, and there is the effect of "supercooling," presumably associated with the energy necessary for setting up a center from which superconductivity can be propagated.

It is proposed to try small alternating fields superimposed on a constant magnetic field around the critical value to investigate the possibility of isolating the phenomena associated with the magnetic transition from the superconducting to the normal state.

F. The Forces Involved in Moving Superconductors in a Magnetic Field
Dr. W. V. Houston, Department of Physics

Objectives:

To study the time dependence of the forces on a moving superconductor.

Report:

Two types of experiments on the forces involved in moving a superconductor in a magnetic field have indicated that there are both conservative and dissipative forces, even in a thin film when no significant eddy current dissipation is observable. The results also suggest an almost continuous transition between a macroscopic intermediate state for a thick strip of the superconductor to an almost uniform distribution of flux in a very thin film. The dissipative force is possibly associated with the electrical resistance observed in other types of experiments.

Experiments are being continued with improved equipment in the hope of making the results more quantitative.

G. The Electromotive Force Associated with the Penetration of the Current and Magnetic Fields Into Superconducting Wires Carrying Alternating Currents
Dr. W. V. Houston, Department of Physics

Objectives:

To study the time dependence of the A.C. losses in a superconductor.

Report:

A longitudinal magnetic field applied to a superconducting wire carrying a current appears to increase the critical current quite

significantly. A 400-cycle generator is now installed and ready for operation, and it is proposed to investigate the frequency dependence of the power loss associated with currents of the superconducting wires.

H. Crystal Optics of Mössbauer Gamma-rays
Dr. C. T. Trammell, Department of Physics

Objectives:

To develop quantum theory of propagation and diffraction of photons in a crystal of resonant scatterers and absorbers.

Report:

The theory has been elaborated over that reported upon last time to take proper account of polarization effects, Zeeman splittings of the nuclear levels, and the interference of electron and nuclear scattering. Using the Feynman techniques of Q.E.D. we develop the theory of the interaction of Mössbauer gamma-rays with crystals containing resonant nuclei. The optics of the 14.4 keV Fe^{57} gamma-ray has been developed in detail, account being taken of the interference of the electronic and nuclear scatterings, the Zeeman splittings of the nuclear levels, and the effect of virtual photon-phonon exchanges between the scatterers. Some novel magneto-optical properties are obtained for ferromagnetic and antiferromagnetic crystals. The theory is applied to the analysis of the available experimental data.

Future plans include an investigation into the feasibility of the use of Mössbauer gamma-rays for making holograms which will then be illuminated with laser radiation to form a magnified image.
The use of Mössbauer gamma-rays in x-ray structure determinations wherein the controllable amplitude and phase of the resonantly scattered gamma-ray should determine the phase of the structure factor is to be investigated.

I. Theory of Magnetism of the Rare Earths
Dr. G. T. Trammell, Department of Physics

Objectives:

To investigate the fundamental indirect exchange mechanism in the rare earths metals, and to develop a theory of the rare earth compounds.

Report:

With a free electron model for the conduction band the isotropic and first order non-isotropic terms of the indirect exchange interaction in the rare earth metals have been calculated exactly (in second order

perturbation). The results are compared with previous treatments of the problem, all of which utilize some type of approximation, and specifically with the calculation of Kaplan and Lyons who assume that the exchange integral $\mathcal{J}(\underset{\sim}{k},\underset{\sim}{k}')$ depends only on $\underset{\sim}{k}-\underset{\sim}{k}'$. It is found that the exact calculation leads to results in disagreement with the approximate treatments: The non-isotropic term is about 4 times larger than that of (KL), and the radial dependence of the interaction is significantly different. The resulting Hamiltonian predicts a ferromagnetic ordering pattern for Gadolinium at $0^{o}K$, while the approximate theories predict a screw structure. However, the predicted ordering pattern for Gd is extremely sensitive to changes in K_F (the Fermi wave vector). (A 5% increase in K_F stabilizes a screw structure with a turn angle of 20°.)

An estimate is given of the relative contribution of the anisotropic term (relative to the isotropic) for the ferromagnetic ordering pattern. For the two-ion asymptotic interaction this effect is found to be quite large, ranging from 40% to 250% among the heavy rare earths and over the values of K_F considered. After being summed over the lattice, the contribution is cut down by roughly an order of magnitude, but the exact amount by which it is reduced is extremely sensitive to the value of K_F.

J. Magnetic Properties of Insulating Crystals
Dr. H. E. Rorshach, Jr., Department of Physics

Objectives:

This research is an experimental investigation of the influence of paramagnetic impurities on the nuclear relaxation time of an insulating crystal.

Report:

One paper on the measurement of nuclear relaxation times has recently been published. Another is in preparation. It will contain a rather complete account of the influence of rare-earth ions on the nuclear relaxation in CaF_2. Experiments presently in progress are directed toward a direct A.C. measurement of the susceptibility of the paramagnetic impurities (g-factor measurements).

K. Magnetic Breakdown in Metals
Dr. H. E. Rorschach, Jr., Department of Physics

Objectives:

This work is a theoretical investigation of the phenomenon of magnetic breakdown for the soluable model of a two-dimensional lattice.

Report:

A theoretical paper on magnetic breakdown has been prepared and submitted to Physical Review for publication.

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

Objectives:

To study the electrostatic potential, field and field gradients in diffused P-N cells, the effect of dimensions on the quantum efficiency of radiant energy cells, and the optimization of the grid structure of solar cells.

Report:

Using the potential field and field gradients in diffused cells, obtained earlier, quantum efficiency has been computed. The results obtained are in agreement with the experimental data in the literature. It has thus been established that the effect of an electrostatic field gradient is much stronger than radiative and non-radiative recombination.

The efficiency of a radiant energy cell could be enhanced by optimizing the dimensions. A study here has resulted in a general expression for the efficiency of the cell for any source temperature in terms of dimensions of the cell.

The grid structure of solar cells has been optimized by setting up a distributive-circuit-element model consisting of a chain of T elements. It is made up of series and shunt paths. For a given cell, the parameters used in the model can be obtained by measuring potential profiles along the length of the cell under three different conditions. The model has been successfully employed to compute optimum gridding of cells. Future plans call for fabrication of cells and optimization of the dimensions and the study of the grid structure in circular cells.

M. Microwave Properties of Ferroelectric Materials
Dr. L. E. Davis, Department of Electrical Engineering

Objectives:

To measure permittivity and loss as a function of temperature in selected ferroelectric materials at frequencies of 2-4 Mh.

Report:

A final sample holder has been designed and constructed. Dielectric

materials of known permittivity have been obtained for the purpose of calibration of the apparatus, but calibration has not been achieved owing to difficulties in machining the samples. After satisfactory calibration of the apparatus, measurements of permittivity and loss tangent of selected ferroelectric materials will be made.

N. Properties of Ferromagnetic Thin Films

Dr. H. C. Bourne, Department of Electrical Engineering

Objectives:

To investigate the properties of ferromagnetic thin films with particular reference to the effect of deposition parameters on loss mechanisms, switching properties, domain behavior, and anisotropic characteristics.

Report:

Measurements of dispersion and flux reversal in the microsecond region indicate considerable sensitivity to deposition and annealing conditions. They were found to form a reasonable basis for evaluation of film performance. The fast pulse system has been used to measure the thresholds of the transition region where the flux reversal changes from wall motion to rotation. The width of the region was found to correlate well with dispersion for the single film for which these measurements have been performed. A digital computer program has been developed for theoretical calculations of film switching equations and has been used to calculate film response with damping of the Landau-Lifschitz type.

Additions to the Kerr-magneto-optic effect apparatus for static domain pattern observation have included earth-field canceling coils, film switching coils and drive circuits. The semi-static domain-wall switching process has been observed both during application of low-level D.C. fields and higher level pulsed fields.

The torque magnetometer has been essentially completed.

Anisotropy of nickel-iron films of 82 percent Ni, 18 percent Fe, has been further investigated. A mathematical model was developed to explain the variation of anisotropy when ridges are formed along or normal to the easy axis. The numerical calculation of this model corresponded to the experimental results. Therefore, a method has been obtained of using demagnetizing effects to adjust the anisotropy of thin film.

The hysteresis-loop tracer has been used to measure dynamic energy losses from 500 c.p.s. to 50,000 c.p.s. for a large group of films. Within this group there were wide variations in film parameters such

as composition and manufacturing conditions. The frequency range was sufficient to cause magnetization reversal by domain wall motion and incoherent rotation. Measurements were made over a temperature range from 25°C to 200°C. Sufficient data were obtained to imply that dynamic energy losses in the domain wall motion mode are due to an intrinsic relaxation mechanism and not eddy-currents. However, in the incoherent rotation region it was found that dynamic losses vary inversely with resistivity. This suggests that either eddy-current losses are significant for this mode of magnetization reversal or that a different type of relaxation mechanism exists which depends on film properties in the same manner as resistivity.

The fast pulse equipment will be redesigned to permit easier measurements. Computer solutions of switching equations based on additional models will be obtained. A closed circuit TV system will be developed for use with the Kerr-magneto-optic apparatus. The torque magnetometer will be completed in the near future and studies initiated with this instrument.

II. Physical Metallurgy

A. 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 and Aerospace Engineering and Materials Science

Objectives:

To obtain detailed knowledge with respect to the effects of solute atoms upon damping loops in magnesium single crystals, to correlate the results with existing theories related to these damping loops, and to investigate the effect of a bias stress upon unidirectional damping loops.

Report:

The critical experiment to test if the memory effect is due to selective dislocation pinning during the creep bias has been performed. Very long term creep stress bias tests on either the loading or unloading portions of the damping loop have shown that under these conditions the memory effect is observed at a constant strain, both upon loading and unloading. It is concluded that the same dislocations do play a role during loading and unloading in the unidirectional damping loop region. The memory effect and ageing studies of the elastic limit which have been carried out in this study can be rationalized in the light of dislocation pinning. At fixed geometrical positions on the slip plane, the bowed dislocations (due to the + and - line tension force) become pinned, but the breakaway stress depends upon whether the dislocation segment experiences a + or - line tension force.

A preliminary analysis of the effect of the solute atoms which have been studied in this program upon the flow stress of magnesium single crystals has been carried out. It appears the solutes per se do not control the low-temperature flow stress but their principal effect is to alter the forest dislocation density. This accounts for the increase in the internal stress and the stronger temperature dependence of the flow stress for the more impure crystals.

Present plans are to write up the results of this study for publication now that a reasonable model to explain the results has been evaluated. Part of the results of this study will be presented in an invited paper at the ASM Symposium on Precision Mechanical Property Measurements June 26-July 1, 1966 in Atlantic City, New Jersey.

B. Microcreep in BCC Metals

Dr. J. M. Roberts, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To gain a better understanding of the strong temperature dependence of the flow stress in b.c.c. metals; to correlate the microcreep and microstrain characteristics with the flow stress characteristics in b.c.c. metals.

Report:

A tantalum single crystal has been grown. Special orientations are being selected. In the light of recent theoretical work done on the cross-slip of screw dislocations in b.c.c. metals by B. Escaig, at the University of Paris, Orsay, France, it is evident the microstrain and microcreep characteristics of b.c.c. metals should be studied after prestrains between 10^{-4} to 10^{-2} at temperatures below 200°K and above. Also it is desired to see if the microcreep characteristics of prestrained Ta and Nb are different from those of Mo since the extent of stage I in the former at low temperature appears to be greater than for comparable purity Mo.

C. Ultrasonic Attenuation of LiF Crystals Between 2°K and 300°K

Dr. J. M. Roberts, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To study in detail the overdamped dislocation resonance peak in LiF crystals between 77°K and 300°K, and to investigate electron damping of dislocations in prestrained Nb and Ta in the normal and superconducting states.

Report:

Anelastic studies in the megacycle frequency range are being carried out to differentiate between the kink chain and string models for the dynamic description of oscillating dislocation.

The dislocation resonant peak in deformed LiF at room temperature has been observed and its position agrees favorably with published results. Attenuation is being measured to $\pm$ 2% and dynamic modulus to $\pm$ 1% with and without static stress bias. No modulus or attenuation change has been observed with resolved shear stress bias tests up to 0.8 of the yield stress. These preliminary results favor the string model of dislocation.

Attenuation and modulus measurements can be made in the frequency range 5 to 100 Mc at this time. It is planned to extend the existing facility to cover the range 150 to 300 Mc. Simple circuits will also be built to allow the modulus to be measured to $\pm$ 0.02% accuracy using the pulse-superposition technique developed by McSkimin. The stress bias experiments will be checked with higher accuracy measurements, and attempts to carry out accurate experiments at 4°K will be made. Improved bonding techniques and shorter samples should yield more accurate attenuation data.

D. Dislocation Damping Mechanisms in the Decrement Region 10^{-3} to 10^{-1} at Low Frequencies (~ 10^{-1} cps)

Dr. J. M. Roberts, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To investigate in detail the effect of dislocation-dislocation interactions upon the low frequency internal friction, to extend these concepts to explain the effect of bias stress upon damping loops observed at low frequencies in Cu, Mg and Zn for example, and to evaluate critically the true meaning of the frictional stress derived from low frequency damping studies.

Report

The amplitude-dependent internal friction at low frequencies determined in this laboratory has been thoroughly analyzed in the light of dislocation-dislocation interactions at repulsive junctions as discussed by Alefeld (cited in Status Report #13). The data can be explained in a quantitative manner by the superposition of five relaxation mechanisms, the activation energies and volumes of which are approximately:

H $\simeq$ 0.50 ev.	V $\simeq$ 1 x 10^{-19} cm^3
H $\simeq$ 0.55 ev.	V $\simeq$ 1 x 10^{-19} cm^3
H $\simeq$ 0.60 ev.	V $\simeq$ 1 x 10^{-19} cm_3
H = 0.67 ev.	V = 7 x 10^{-20} cm^3
h= 0.77 ev.	V = 1 x 10^{-20} cm^3

These values explain the broad relaxation peak at 240°K at low stress, and a smaller peak at 270°K which does not shift with stress amplitude. These values also explain correctly the stress dependence of the peak temperature as well as the shift with frequency of the latter. The microscopic work-hardening coefficient acting upon dislocation has been evaluated and is reasonably related to the experimentally observed damping loop and also is compatible with a 10% modulus defect at zero stress.

The mechanism of the hysteretic breakdown of attractive dislocation junctions has been considered in detail. Most of the junctions break down by the triple nodes moving together with the subsequent formation of two jogs, and no point defects are expected to be formed. Allocation of this model to amplitude-dependent hysteresis has been carried out. This theory explains quantitatively most of the results obtained in this laboratory upon copper single crystals.

E. The Temperature Dependence of the Flow Stress-Work-Hardening Coefficient and Activation Volume in Cadmium Single Crystals

Dr. J. M. Roberts, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To obtain a better understanding of the work-hardening characteristics of easy glide in hexagonal close-packed metals.

Report:

The work-hardening coefficient of zinc single crystals deformed in shear to strain of about 0.60 is being measured between 77°K and 300°K. If a maximum in the work hardening coefficient at 270°K is found for zinc in shear (as is indicated by the tensile tests of Trauble and Seeger), then indirect confirmation of the maximum found for cadmium in this laboratory will result. Reproducibility of the work-hardening coefficient by straining, reverse straining and annealing of zinc crystals in shear is now being established. Once this is done, the temperature dependence of the work-hardening coefficient can be measured.

F. Electrical Resistivity of Deformed Molybdenum Single Crystals

Dr. F. R. Brotzen, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To study the dislocation multiplication in molybdenum single crystals.

Report:

Several molybdenum crystals were deformed at room temperature to a total tensile strain of approximately 10%, and the deformation was continued subsequently at a lower temperature. The electrical resistivity at 4.2°K was measured for this deformation procedure. It was noted that the slope of the resistivity as a function of strain was lower at the higher deformation temperature. Subsequent straining at low temperatures led to a resistivity curve which

approached the relatively steep slope characteristic of that low temperature. This was interpreted as a gradual rearrangement of the defect structure to the point of reaching a dislocation distribution characteristic of the deformation temperature.

G. Mechanical Properties of Molybdenum Single Crystals
Dr. F. R. Brotzen, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To evaluate the effect of small amounts of impurities on the mechanical properties of molybdenum single crystals.

Report:

The effects of various parameters in the electron-beam zone refining of molybdenum on the purity of the single crystals have been evaluated. The purity of the single crystals has been found to increase with:

Increased purity of the starting material;
Increased vacuum during the growing process;
Increased number of zone passes.

Low value longitudinal electrical fields were found to have no detectable effect on the purity of the single crystals. Because of the very high purity of all of the single crystals, the electrical resistivity at $4.2^{\circ}K$ was taken as an indication of the purity of the crystals. Single crystals with $R_{273/4.2}$ between 700 and 7300 were grown and tested in direct shear over the temperature range of $78^{\circ}K$-$400^{\circ}K$. The effects of impurities were found to be temperature dependent. Below $300^{\circ}K$ the impurities contributed to the formation of obstacles which could be overcome by the thermal activation of the dislocations. Above $300^{\circ}K$ increased purity or decreased strain rate permitted the detection of features in the stress-strain curves which are characteristic of the three-stage stress-strain curves often obtained for the f.c.c. metals. Detailed results are included in a Ph.D. thesis.

H. Direct Observation of Dislocations in Molybdenum
Dr. F. R. Brotzen, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To observe directly the variation of dislocation density with strain in the region 5% to 40% shear strain at $300^{\circ}K$, $195^{\circ}K$ and $78^{\circ}K$.

Report:

Single crystals of molybdenum were strained in direct shear on $(1\bar{1}0)$ planes along the [111] direction. Crystals were sheared to approximately 5, 10, 20, and 40 per cent shear strain at 195°K, 300°K, and 373°K, and 2 to 6 per cent shear strain at 78°K.

Specimens taken from the $(1\bar{1}0)$ shear plane were examined in transmission electron microscopy. The dislocation structure was examined at each strain and temperature increment, and measurements of the dislocation density and the density of jogs on primary screw dislocations were made. The results indicated that:

1. The dislocation density of molybdenum single crystals deformed in shear increases with strain at all temperatures investigated except 300°K.

2. This increase in ρ was linear, and as the deformation temperature is lowered, the rate of increase is accelerated.

3. The density of jogs on primary screw dislocations varies with strain and temperature much as does the dislocation density.

4. Conservative motion of jogs on screw dislocations becomes appreciable above 300°K.

5. The ease and scale of cross-slip of screw dislocations increases with increasing temperature.

6. The amount of secondary slip in crystals oriented for direct shear on $(1\bar{1}0)$ planes increases as deformation temperature decreases.

7. At 195°K and 300°K, the proportion of edge dislocation length to screw dislocation length increases as strain and tangling increase.

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

Objectives:

To relate the electrical resistivity of a binary alloy to the state of short-range-order (SRO) by both theoretical and experimental means.

Report:

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 monocrystals. 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 be measured, over the range of 4.2 to 300°K.

This topic is important to the understanding of materials because nearly 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.

A doubly bent crystal monochrometer and a single crystal orienter have been installed on the x-ray diffractometer, and the alignment has been completed. A device to maintain the x-ray sample at cryogenic temperatures has been constructed to correct for the temperature diffuse scattering. Also, to improve the accuracy of the x-ray measurements, a detector has been installed to monitor the x-ray source and an additional scaler has been incorporated as a "slave" to the regular counting equipment. A computer program for the analysis of the data has been written and "debugged".

A portion of the reporting period has been devoted to preparing a suitable crystal for examination. A Pd-Au single crystal was purchased and a surface has been cut within 1/2° of a {100} plane, and a smooth, strain free surface prepared.

There has been a controversy concerning the theoretical basis of diffuse scattering of x-rays. Hence, during this reporting period, a systematic development of this theory has been accomplished and has been accepted for publication.

Experience from this project has shown that the existing x-ray diffraction laboratory, equipped by University funds and industrial grants, could not support both a long term research project and teaching. Hence, some funds were used from this grant, along with University funds and some industrial grants, to expand the facilities to include an additional diffractometer and associated counting equipment.

J. Electron Microscope Facility and Thin Film Research

Dr. M. L. Rudee, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To provide a well equipped electron microscope laboratory for the use of various research projects and teaching at Rice University.

Report:

The electron-microscope facility in the materials group at Rice includes a Philips EM-200 electron microscope, various accessories for the examination of crystalline materials, a well-equipped specimen preparation facility, and a dark room.

During this reporting period equipment was added to support the increased volume of dark room work. In addition, the existing vapor deposition equipment has been improved by adding a feed-through collar.

There were four main research programs utilizing the electron microscope:

1. The examination of dislocation density and arrangement in deformed molybdenum single crystals;

2. The observation of radiation damage in silicon (an NSF project);

3. The evaluation of the structure of magnetic thin films (this topic is discussed in greater detail below);

4. Analysis, by means of selected area diffraction, of the periodicity in calogen found in certain kidney tissue (in cooperation with Dr. John Sharp of Baylor College of Medicine).

In addition, four graduate students received enough laboratory experience using the electron microscope to be able to utilize this technique independently on their own research.

A project investigating the structure-property relationships in permalloy thin films has been initiated. This will be accomplished in close cooperation with a group in the Electrical Engineering Department. It is envisaged that a careful research of this nature will increase the understanding of the behavior of these devices.

Films will be produced under various well-defined conditions and their magnetic properties (anistropy constant and anistropy dispersion) measured. The structure of the films will then be characterized by the following methods.

1. Particle size and strain by Warren-Averbach x-ray peak shape analyses;

2. Grain size by normal electron microscopy;

3. Magnetization ripple by Lorentz microscopy.

During this reporting period techniques for all the abovelisted procedures have been developed. The computer program for the x-ray analysis has been written. Accumulation of data should progress in the next reporting period.

Additional laboratory space will be acquired that will expand the specimen preparation area and allow an improvement in these facilities. Data accumulation on the thin magnetic films will commence.

K. An Investigation of the Energies and Entropies of Solute Atoms in Dilute Solid Solution

Dr. R. B. McLellan, Department of Mechanical and Aerospace Engineering and Materials Science

Objectives:

To establish experimental values for the partial energies and entropies in solutions dilute enough so that solute-solute interactions can be neglected or treated theoretically.

Report:

The partial energies and entropies for dilute substitutional alloys will be measured by a Knudsen cell method. The apparatus is now partially constructed - the furnace is complete and work is now proceeding on the vacuum system.

A project is also underway to extend the investigator's previous calculations on dilute interstitual solutions to more concentrated solutions by introducing a repulsion interaction between solutes which is a function of concentration. The computation of the degeneracy and thus the entropy of the solution crystal has been made using successive ensemble averaging techniques. A closed expression for the free energy has been found and the results will be applied to the C - gamma iron system.

III. Chemistry of Solids

A. Hard Sphere Solids and Anharmonic Forces in Real Crystals

Dr. Z. W. Salsburg, Department of Chemistry

Objectives:

With the advent of new experimental results on the high temperature, high pressure properties of solids, there has in the last few years been a renewed interest in the theory of anharmonic properties of solids. The usual method of treating anharmonic effects by perturbation theory is not valid under very high temperature and pressure conditions where anharmonic forces play a dominant role in the thermodynamic and elastic properties. The approach taken to this problem is to consider the properties of a hard sphere solid as a leading approximation and then introduce the effects of attractive forces and softer repulsions by perturbation theory.

Report:

1. Free Energy of Vacancy Formation in Solids

A theory was developed for calculating the equilibrium concentration of monovacancies and divacancies in a highly anharmonic solid and applied to a model of rigid disks and rigid spheres. This theory predicts a concentration of .0008 for monovacancies and .000 0008 for divancancies (in vacancies per lattice site) for rigid disks at a density .8 of the close-packed density. The corresponding concentration of monovacancies in a rigid sphere system at .8 of the close packed density is predicted to be .000 016 (Note: computer calculations indicate that a rigid disk solid melts at a density equal to .8 of the close packed density.)

2. A Modified Cell Cluster Theory

A modified cell cluster theory for calculating the specific free energy of a solid was applied to a harmonic model of a perfect monatomic crystal corresponding to the two dimensional triangular lattice with nearest neighbor interactions only. This technique starts with the single particle (Einstein) theory and then evaluates corrections from correlated motion of larger and larger sets of contiguous particles. In the high temperature limit the general harmonic theory leads to an expression for the Helmholtz free energy, F_N, in the form,

$$F_N/NkT = -2 \ln T^* + D_N$$

with $T^* = kT/h\nu_0$. For the Einstein model $D_N = 1.0986\cdots$ while the modified cell cluster technique carried through sixth order gives $D_N = 0.8565\cdots$. The technique is also applied to a one dimensional

harmonic model. From these and earlier studies we were led to the conclusion that a cell cluster theory is an appropriate method for treating anharmonic forces in a solid particularly at high temperatures and pressures.

3. Relative Stability of Face Centered Cubic and Hexagonal Close Packed Structures

The entropy effect due to anharmonic forces for the face centered cubic structure and the hexagonal close packed structure was investigated. There appears to be a stabilization of the hexagonal structure by anharmonic forces and this indicates possible high temperature transitions in the noble gas solids. Such transitions have not been observed or investigated experimentally.

4. Radial Distribution Function in High Density Rigid Sphere Systems

A technique, modeled after the cell-cluster theory for the partition function, was developed for estimating the molecular pair distribution function. This technique while general is thought to be particularly applicable to high density crystalline systems. Attention is focused on $\Omega(\zeta)$, the average number of pairs that have a distance between centers less than or equal to ζ. In the high density crystalline limit $\Omega(\zeta)$, for a system of N μ-dimensional rigid spheres, has the following expansion

$$2\Omega/N = 2\mu\eta + b\eta^2 + c\eta^2 + \cdots$$

$$\eta = (\zeta - \sigma)/(a - \sigma)$$

where a is the distance between lattice sites and σ is the diameter of a sphere. The exact development for a one-dimensional system is given whereby the technique can be demonstrated to be convergent. For two-dimensional rigid disks all contributions from four particle or fewer cell-clusters to the constant b were calculated. The resulting series through fourth order is

$$b \approx 2 - \frac{192}{217} - 1.6069 + 0.2599 + \cdots \quad .$$

5. The Elastic Constants for High Density Anharmonic Solids

Corresponding to the theories described above an analogous theory for the elastic constants of a hard sphere solid has been developed. This will help clarify the deviations from the Cauchy relations observed experimentally at high temperatures and pressures. As a sample calculation we have evaluated the single shear modulus for a two dimensional hexagonal system of rigid disks. We are currently computing the three elastic constants for a face centered cubic system of rigid spheres and the six elastic constants for a hexagonal system of rigid spheres.

6. Statistical Mechanical Properties of Small Systems in the Isothermal-Isobaric Ensemble

The exact N dependence was found for the first N-1 virial coefficients calculated for a system with a finite number, N, of particles in the isobaric-isothermal ensemble. When the specific volume $v = V/(N+1)$ is expanded as a power series in $z = p/kT$, it is shown that the first N-1 coefficients are linear functions of $(N+1)^{-1}$. The explicit results are given for the first six coefficients.

7. Voids in a Crystal Structure of Identical Spheres

A technique (primarily for pedigogical purposes) has been developed for determining the size and location of all interstitial spheres in a regular crystalline structure. This provides a convenient algebraic method by which one can obtain these results without any recourse to pictures or geometrical considerations.

8. Rigid Disks and Spheres at High Densities: Bounds on the Partition Function

Upper and lower bounds on the partition functions for finite systems of N rigid disks and N rigid spheres are obtained for the high density limit. The lower bounds are also valid in the thermodynamic limit of $N \to \infty$ and at all densities. Consider the following asymptotic form for the specific Helmholtz free energy for a classical mechanical system of N ν-dimensional (ν=2 or 3) hard spheres confined in a volume V in the limit $V \to V_0$ (the close-packed volume),

$$A_N/Nk_BT \cong + \nu \ln \frac{\Lambda}{\sigma} - \nu \ln\left(1 - \frac{V_0}{V}\right) + C_\nu(N)$$

where Λ is the de Broglie wavelength and σ the sphere diameter. The lower bounds obtained for $C_\nu(N)$ are $C_2(N) > -0.7576\cdots$ and $C_3(N) > -0.05074\cdots$. Two upper bounds found for C_2 are $C_2 < 1.289\cdots$. An upper bound for C_3 is $3.6423\cdots$.

Future Plans Include: A continuation of the calculations of the free energy function for hard sphere solids at high densities, the elastic constants of such solids and the radial distribution function. This work uses the cell cluster method. It is also planned to investigate the tunnel model and its extension and re-evaluate the free energy function and radial distribution function predicted by this model.

B. Oxidation of Nickel at Elevated Temperatures
Dr. W. W. Akers, Department of Chemical Engineering

Objectives:

To determine the mechanism of the oxidation process and the effect of

oxidation on the thermal emittance of the surface.

Report:

The rates of oxidation of single crystals and the thermal emittance of these surfaces have been measured. The results correlate quite well with the earlier poly-crystalline studies reported previously. The steps in the oxidative process are: (1) chemisorption, (2) a nucleation stage which follows a logrithmic rate mechanism, (3) a quartic region and (4) a parabolic region. There are no major differences in the rate or mechanism of each of the three principle faces of the crystal. The thermal emittance measurements support the proposed mechanism of the kinetic model.

Future work will follow two routes: (1) oxidation of nickel with a halogen forming a volatile oxidation product, and (2) oxidation of other metals with oxygen to determine if the nucleation step is present.

C. High Temperature Interactions between Gases and Condensed Phases - Kinetic Studies (with Dr. C. H. Williams)
Dr. J. L. Margrave, Department of Chemistry

Objectives:

To utilize microbalance and mass spectrometric techniques for characterizing gas-solid interactions for a variety of materials over wide ranges of temperature.

Report:

The ion source and electronics of a Bendix Model 14 time-of-flight mass spectrometer have been modified to permit studies of the interaction between a molecular beam and a heated metal surface. Several aspects of one system are being investigated currently. A molecular beam of BaF_2, effusing from the Knudsen cell, impinges on the surface of a heated poly-crystalline platinum ribbon, where it dissociates and thermally ionizes to the molecular and atomic ions, BaF^+ and Ba^+, respectively. The work function of the Pt surface has been measured. Negative ions produced in the dissociation-ionization of the BaF_2 will be sought.

When BaF_2, with a molecular beam intensity of 5×10^{10} molecules $sec.^{-1}$ (corresponding to 10^{-2} monolayers $sec.^{-1}$), strikes the Pt ribbon surface at a temperature of 1850°K, BaF^+ and Ba^+ ions desorp from the surface in the ratio 12:1. A semilog plot of the mass analyzed ion current of the largest isotopes of BaF^+ and Ba^+ versus the reciprocal of the Pt surface temperature gives a straight line between 1700-1850°K. The slopes of these linear portions were -4.5 e.v. and -7.5 e.v. respectively for BaF^+ and Ba^+. The slopes should give (φ - I), the

difference between the work function of the Pt surface, φ, and the ionization potential of the adsorbed species I; however, the slopes measured for BaF^+ and Ba^+ were much too large to be accounted for using the literature values[2] (Pt work function = 5.32 e.v.[1], Ionization potential of BaF = 4.9 e.v.[3] and Ba = 5.2[3]).

It appears that other energy terms must be taken into account, e.g., the heat of desorption of the ions.

As a supporting experiment the work function of the polycrystalline platinum ribbon was measured in place in the mass spectrometer. As observed by Whitney[1] and others, the measured work function (and the value of the thermionic constant A) changed as the Pt ribbon was heated in the vacuum system. At one point in the aging process the values φ = 6.80 e.v., A = 3×10^4 amp. cm^{-2} deg^{-2} were measured. With continued heating near the m.p. of Pt these values decrease markedly.

Provisions have been made to search for negative ions formed in the dissociation-ionization process. Future experiments will investigate the emission of positive ions, negative ions (if formed) and electrons from the Pt surface as a function of temperature and Pt work function (i.e. aging) and BaF_2 molecular beam intensity.

The molecular beam experiments with BaF_2 and with other metal halides on hot filaments will be continued and the activation energies, etc. for the various processes evaluated.

D. High Temperature Interaction Between Gases and Condensed Phases - Sublimation Studies

Dr. J. L. Margrave, Department of Chemistry

Objectives:

To utilize microbalance and mass spectrometric techniques for characterizing gas-solid interactions for a variety of materials over wide ranges of temperature.

Report:

Microbalance and mass-spectrometric techniques have been used to establish the identities and stability of vapor species over organic solids and several transition metal and rare-earth fluorides. Rare-earth and transition-metal chelates with 2,2,6,6-tetramethyl-heptanedione are also being studied.

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[1] L. V. Whitney, Phys. Rev. 50, 1154 (1936).

[2] T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).

[3] Introduction to Mass Spectrometry and Its Applications, Robert W. Kiser, Prentice-Hall, Inc., N. J. (1965), p. 302.

Periodic trends in fluoride bond energies have been determined, and the stability of the perfluorosilanes determined by mass spectrometer appearance potential studies.

Microbalance and mass spectrometric studies of sublimation kinetics and equilibria will be conducted, with special emphasis on selected organic molecules and on refractory ternary oxides (silicates, zirconates, etc.)

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

Objectives:

The object of this work is to determine the geometry of several classes of organic molecules and the effects of various functional groups and crystal forces on this geometry.

Report:

The structures of potassium titranitroethide, potassium trinitromethide, and ammonium 1,1,2,6,7,7-hexacyanohepta trienide are presently under investigation. The X-ray data have been collected on all three and the trial structure of ammonium 1,1,2,6,7,7-hexacyanoheptatrienide has been determined. All of these substances are carbanions and constitute a continuation of a program spanning the previous two years.

The solution of the structure of cis-2-butene episulfone has resulted in the observation of an exceptionally long carbon-carbon bond length in the episulfone ring. This feature has been tentatively attributed to hyperconjugation enhanced by the presence of the sulfone group. To test this hypothesis we have initiated a series of structural investigations on small ring sulfones. At present data are being collected on two such molecules. A trial structure has been found for the compound dibenzylthiophene-5,5'-dioxide.

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

Objectives:

To relate catalytic activity on the surface of a powder to the electronic energy shifts induced by monochromatic ultra-violet irradiation of the surface, to compare changes in electrical conductivity and Seebeck EMF induced in compressed powders and in single crystals of the same material brought about by exposure to the same radiation, and to compare catalytic activity perturbed by similar radiation exposure in single crystals and in powders of the same material and study the relationship to the electrical measurements.

Report:

The apparatus to measure reaction rates of CO oxidation over a ZnO single crystal and measure conductivity and Seebeck EMF in the crystal has been completed and calibrated. Some redesigning of the valves and connections has been carried out to allow operation while submerged in the isothermal bath fluid.

The pelletizer to prepare pellets of compressed ZnO powder has been completed. The technique for measuring electrical conductivity and Seebeck EMF in these pellets has been developed. A technique to measure the total dipole energy in the space charge created by chemisorbed ions and the charged surface has been developed and is being tested.

Catalytic activations of MgO powders using monochromatic UV irradiation are being carried out with a modification of the Beckman D^K-U spectrophotometer. An improved reactor has been built to allow each catalytic surface exposed to receive, as nearly as possible, the same dosage. Data are now being taken.

Doped samples of MgO with Fe, Cr, and other metallic ions have been prepared and reproducible catalytic activities are obtained on repeated preparations. Data to compare the doping effect on catalytic activity are now being taken.

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

Objectives:

To study the application of two dimensional equations of state to pure and mixed hydrocarbons on charcoal and silica gel.

Report:

Experimental adsorption data for methane, propane, and n-butane on charcoal have been obtained from 10°C to 70°C at pressures to 2000 psia. Adsorption of mixtures of methane and propane have been studied at 30°C at pressures up to 2000 psia.

The two-dimensional equation of state based on a three dimensional equation for dense fluids proposed by Eyring has been derived and shown to describe the adsorption very accurately in this region for pure hydrocarbons and their mixtures on charcoal.

H. Adsorption of Gas on Solids
Dr. R. Kobayashi, Department of Chemical Engineering

Objectives:

To develop a statistical mechanical theory for adsorption of gas mixtures and to measure adsorption by gas chromatographic or perturbation techniques.

Report:

The notion of an hypothetical infinite temperature perturbation has been introduced in chromatography. The retention volume for such a perturbation is obtained by the extrapolation of the He, Ne, Ar perturbations to obtain the retention volume of a gas of zero mass (infinite temperatures). Using the assumption that such an hypothetical gas will not be adsorbed (or even absorbed) it is now possible to obtain the free gas volume and hence the adsorbed volumes of both permanent and impermanent gases as a function of pressure, temperature, and compositions. Using this technique it is now possible to present adsorption data on an absolute basis and hence discard the unrealistic Gibbs adsorption which presumes that the adsorbed volumes cannot be measured.

Adsorption isotherms and adsorbed volumes on silica gel are being measured for methane, ethane, and several mixtures of methane and ethane using the perturbation technique up to 100 atmospheres or to the pressure limits imposed by the phase transition conditions of the system.

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

Objectives:

To predict hydrate formation conditions and hydrate composition for non-spherical molecules, and to prepare an apparatus for the study of hydrate compositions.

Report:

Experimental equipment for the determination of the hydrate numbers as a function of pressure, temperature, and phase compositions has been completed. Preliminary experimental runs will be made in the near future. The hydrate numbers will be used to test the internal consistency of the statistical mechanical theory of gas hydrates.

APPENDIX I

PUBLICATIONS DURING THE PERIOD OF THIS REPORT

R. B. Hemphill, P. L. Donoho, and E. D. McDonald
"Spin-Lattice Interaction in Ruby Measured by Electron Spin Resonance in Uniaxially Stressed Crystals"
Accepted for publication by Phys. Rev. 146, No. 1 (to appear June 3, 1966).

M. P. Maley, H. A. Blackstead, and P. L. Donoho
"Microwave Magnetoelastic Effect in Thin Films of Dy, Ho,Gd, and Er"
Published J. Appl. Phys. 37, 1006 (1966).

W. V. Houston and David R. Smith
"Mechanical Forces on a Superconducting Film"
Published Phys. Rev. Let. 16, 12 (March 1966)

Y. Kitano and G. Trammell
"Heat Magnetization"
Published in Phys. Rev. Letters, (March 28, 1966)

W. G. Chambers
"Magnetic Breakdown: Effective Hamiltonian and de Haas-Van Alphen Effect"
Submitted to Phys. Rev.

R. Burnett
"^{19}F Nuclear Relaxation Time in CaF_2:Nd"
Published in Physica 32, 433 (1966)

G. C. Jain and Seng-Shen Li
"Effect of Dimensions On the Quantum Efficiency of Radiant Energy Cells"
Published IEEE Trans. on Aerospace (March 31, 1966)

G. C. Jain and R. M. S. Al-Rafai
"The Effect of Electrostatic Field Gradient in Semiconductors with Diffused Impurities"
Accepted for publication J. App. Phys., May 1966

H. C. Bourne
"Modified Method of Measuring Dielectric-Constants Using a Rectangular Cavity-Resonator"
Submitted to Trans of I.E.E.E on Instrumentation and Measurements.

T. Ishibachi and M. L. Rudee
"Singularities in the Coherent Diffuse Scattering of X-Rays)
Accepted for publication J. App. Phys.

Z. W. Salsburg, W. Rudd et al
"A Modified Cell-Cluster Theory for the Solid State with Application to the Harmonic Model"
Accepted for publication by Physica

Z. W. Salsburg
"Statistical Mechanical Properties of Small Systems in the Isothermal-Isobaric Ensemble"
Published J. Chem. Phys. (April 15, 1966)

Z. W. Salsburg
"Voids in a Crystal Structure of Identical Spheres"
Submitted to J. Chem. Ed.

Z. W. Salsburg
"Rigid Disks and Spheres at High Densities: Bounds on the Partition Function"
Accepted for publication J. Chem. Phys.

Z. W. Salsburg and W. G. Rudd
"The Tunnel Model for Rigid Disks near Close-Packing"
Submitted to J. Chem. Phys.

J. L. Margrave and K. F. Zmbov
"Mass Spectrometric Studies at High Temperatures. XI. The Sublimation Pressure of NdF_3 and the Stabilities of Gaseous NdF_2 and NdF"
Submitted for publication, J. Chem. Phys.

K. F. Zmbov and J.L. Margrave
"Mass Spectrometric Studies at High Temperatures. XII. Stabilities of Dy, Ho and Er Sub-fluorides"
Submitted for publication J. Am. Chem. Soc.

K. F. Zmbov and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. XIII. Stabilities of Samarium, Europium and Gadolinium Mono- and Difluorides"
Submitted for publication J. Inorg. and Nucl. Chem.

J. D. McDonald, J. C. Thompson, C. H. Williams and J. L. Margrave
"Silicon-Fluorine Chemistry V. Appearance Potentials and Thermo dynamic Prioerties for Si_2F_6, Si_3F_8, Si_4F_{10} and $SiBF_7$"
Submitted for publication J. Am. Chem. Soc.

"Proceedings of Conference on Current and Future Problems in High Temperature Chemistry" edited by J. L. Margrave
Accepted for publication, National Research Council, Washington, D. C.

Characterization of High Temperature Vapors
Ed by J. L. Margrave. In press, J. Wiley & Sons (New York) (1966)

J. L. Margrave and R. A. Kent
"Mass Spectrometric Studies at High Temperatures. VIII. The Sublimation Pressure of Iron (II) Fluoride"
J. Am. Chem. Soc. 87, 4754 (1965)

J. L. Margrave
"Binding Energies in Binary Fluorides"
Bull. Am. Phys. Soc. 10, 704 (1965)

A. S. Kana'an, G. Besenbruch and J. L. Margrave
"Knudsen and Langmuir Microbalance Measurements of the Sublimation Pressure of CoF_2"
Accepted for publication J. Inorg. and Nucl. Chem.

R. A. Kent, J. D. McDonald and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. IX. Sublimation Pressure of Cu (II) Fluoride"
J. Phys. Chem., 70, 874 (1966)

B. D. Kybett, P. Natalis, J. L. Franklin, D. Bonnell and J. L. Margrave
"Thermodynamic Properties of Cubane"
J. Amer. Chem. Soc., 88, 626, (1966)

R. A. Kent, J. D. McDonald, A. S. Kana'an, and J. L. Margrave
"Sublimation Pressures of Transition Metal Fluorides"
Proc. Symp. on Non-fissionable Ceramics, Am. Nucl. Soc., May 9-11, 1966, Washington, D. C.

A. S. Kana'an, G. Besenbruch and J. L. Margrave
"Mass Spectrometric Studies at High Temperatures. X. Sublimation Pressures of Sc(III), Y(III) and La(III) Trifluorides"
Accepted for publication, J. Inorg. Nucl. Chem.

Robert Desiderato and R. L. Sass
"The Crystal Structore of cis-2-butene Episulfone"
Submitted for publication Acta Cryst.

John J. Haydel and R. Kobayashi
"Adsorption Equilibria in the Methane-Propane-Silica Gel System"
Paper submitted to J. Chem. & Eng'g Data (A.C.S.)

I. Nagata and R. Kobayashi
"Prediction of Dissociation Pressures of Mixed Gas Hydrates from Data for Hydrates of Pure Gases with Water"
Paper submitted I. E. C. Fundamentals