Faculty

UNPUBLISHED PRELIMINARY DATA

WILLIAM MARSH RICE UNIVERSITY

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Semiannual Status Report #11

On

NASA RESEARCH GRANT NO. NsG-6-59

Covering

Research on the Physics of Solid Materials

For the Period

1 May 1964 through 31 October 1964

Under the Direction

Of

Franz R. Brotzen

The funds expended under this grant are used for the promotion of fundamental research in the field of physical behavior of solid material and, at the same time, for the stimulation of graduate education of scientists and engineers. The Rice University has endeavored to pursue these goals in the 6 years during which this grant has been active.

Progress made in the past 6 months in the research of 33 different projects is reported. These research projects are directed by 16 chief investigators, all of whom are faculty members in 6 different departments of the University. As a result of their common interest in materials research, cooperation between investigators of different departments has increased substantially. The work done under this grant has led to the preparation of a number of manuscripts and the publication of several papers, all of which are listed in the report.

Although the research performed under this grant is of a fundamental nature, its application to certain real problems is evident in many instances. For example, much of the work done on paramagnetic spin resonance has a bearing on maser and laser problems. The work done by various groups at the Rice University in the field of magnetic properties is basic to the development of new magnetic materials. Investigations of lattice defects in metals and other solids have already led to the creation of materials with promising mechanical properties. Similarly, the study of transformations and their kinetics is essential to the development of heat treatments

of alloys. Research on thermodynamic properties of solids is of particular interest to the development of materials for high temperature applications, and the basic information gained from the study of surface properties has, of course, far-reaching consequences on certain materials at elevated temperatures.

In the course of the past 6 months a total of 37 graduate students worked on projects sponsored by this grant. Most of these students are candidates for a doctors degree. In addition, a few undergraduates were also employed as part-time technicians on some of the research projects listed in this report. There are 7 post-doctoral fellows working on various projects sponsored by this grant.

I. Solid State Physics

A. Paramagnetic Spin-Lattice Interactions

Dr. P. L. Donoho, Department of Physics

Work on the effect of uniaxial stress on the ESR spectrum of ruby was completed, with very much better results than obtained in the preliminary work reported earlier. The results of this work are being reported in a paper to be submitted to Physical Review. Further work on spin-lattice relaxation in ruby is being completed and will be reported in preliminary form at the December 1964 Am. Phys. Soc. meeting in Berkeley. Work on CaF_2 doped with rare earths is proceeding. Relaxation measurements are presently being carried out, whereas some uniaxial stress measurements have been completed and are being prepared for publication.

B. Phonon-Phonon Interactions

Dr. P. L. Donoho, Department of Physics

Very good preliminary results have been obtained on phonon-phonon interactions through the study of microwave-ultrasonic absorption in CaF_2. Both experimental and theoretical work is being carried out in this area. Preliminary results were reported at the June 1964 Am. Phys. Soc. meeting in Denver.

C. Phonon-Magnon Interactions

Dr. P. L. Donoho, Department of Physics

Generation of ultrasonic waves through spin-wave resonance in ferromagnetic thin films is being studied. It is hoped that a careful quantitative investigation will yield useful information on spin-lattice couplings in ferromagnets.

D. Superconductor Tunneling Junctions

Dr. P. L. Donoho, Department of Physics

A program is underway to study the interactions between tunneling supercurrents and radiative fields, both photons and phonons. Both theoretical and experimental work have been started, but no experimental results have yet been obtained. Most work to date has been concerned with the production of good tunneling junctions.

E. Laser Research

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

The project of building an apparatus to completely measure the

polarization of the output light of a laser as a function of time has been completed. The system has a time resolution of 10^{-7} seconds. Preliminary measurements have been made on the light from a neodymium glass laser. The effect of externally applied magnetic fields on the polarization of the laser light will also be studied.

This study should result in a better understanding of the lasing process. The effects of externally applied magnetic fields are of interest both as an internal modulation technique and as a means of gaining a better understanding of the interaction of electromagnetic fields in a solid state laser with the paramagnetic ions which generate the laser action.

In addition to the above project, some work has been initiated to develop a laser light source of sufficient intensity to vaporize material to be analyzed in a mass spectrometer. This work is being carried out in cooperation with Dr. J. L. Margrave of the Chemistry Department.

The following paper has been published:

A. S. Badger and T. A. Rabson, "Zeeman Effect and Ruby Laser Polarization", Proc. of the I.E.E.E., 52, 1047, (1964).

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

The work continued the study of the losses in superconducting wires carrying 60 cycle heavy currents. To relate the losses to flux penetration and trapping, the voltage vs. current traces were recorded on an oscilloscope for various d.c. currents which were superimposed on the a.c. currents. The results agreed qualitatively with Bean's model for irreversible flux penetration.

The work also included a solution of the heat-flow equation for current input leads from a high temperature reservoir into liquid helium. Materials with a large thermoelectric figure of merit would be useful for d.c. currents if the high temperature is above 80°K. Superconducting materials between 4.2°K and 18°K would significantly decrease the heat flow to liquid helium only if liquid hydrogen were used.

The work on 60 cycle losses is being continued to investigate flux penetration in more detail.

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

An investigation of the fundamental magnetic ordering interaction mechanism in the rare earth metals has been completed. This work was carried out primarily by F. Specht as his doctoral research problem and represents a quite significant contribution to our understanding of these materials. Briefly, this work reveals that the indirect exchange interaction between rare earths should be quite anisotropic, with corrections to the usual isotropic RKY interaction varying among the rare earths but of the order of several tens of per cent. A report is to be given at the New York American Physical Society Meeting (Jan. 27-30, 1965), the thesis will be submitted in November-December, 1964, and a paper submitted for publication in the Physical Review early in 1965.

The dynamical magnetic properties of rare earth-intermetallic compounds have been investigated. The nature of the "crystal field band" has been found to be the principal determinant of these properties. The spin waves are found to have novel characteristics, consisting of both longitudinal and transverse modes with novel dispersion relations. This work was reported on at the International Conference on Magnetism in Nottingham, England (September 1964), and an expanded version of the talk is to appear in the Proceedings of the Physical Society (London) in early 1965.

The susceptibility of a linear spin chain with nearest and next nearest neighbor interactions has been computed in the Ising model approximation (Kitano). The variation of wave number of maximum susceptibility with temperature is found, and its bearing on the temperature dependence of turn angle in the rare earth metals is investigated. This work is being prepared for publication.

A paper on the Aharonov-Bohm Effect, which represents research reported on in the last semi-annual report, appeared in the Physical Review, Vol. 134, No. 5B, pp. B1183-B1184, 8 June 1964.

H. Nuclear Relaxation in Insulating Crystals
Dr. H. E. Rorschach, Department of Physics

Experiments are in progress to study the nuclear spin-lattice relaxation time of F^{19} in CaF_2 crystals due to the presence of known amounts of paramagnetic impurities. A pulsed nuclear-

magnetic-resonance spectrometer capable of saturating laser-type crystals in the temperature range $1^{o}K$ to $300^{o}K$ has been constructed and used to investigate CaF_2 doped with Uranium, Erbium, Europium, and Samarium. This work is being prepared for publication.

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

A high-vacuum system, ultimately capable of pressures less than 10^{-9} mm Hg, was purchased from Varian Associates. The system arrived during the summer and is in the process of being assembled. Two electron guns together with the power supply are being installed in the system. This vacuum system is being designed specifically for the evaporation of ferromagnetic thin films under various controlled conditions. The system will also be available for other research programs in the general area of solid-atate electronics and materials science.

In addition to the work on the high-vacuum system, the new solid-state electronics laboratory is being put into operation. Major equipment includes a furnace, a 7-inch magnet, and fume hood.

The abstracts for two papers have been submitted for presentation in April 1965.

II. Physical Metallurgy

A. Transmission Electron Microscopy of Au-Co-Alloys

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

Rolled sheets were quenched from 880°C. Efforts were concentrated on the finding of a suitable heat treatment and on an improvement of the specimen preparation technique. Annealing in a salt bath at 400°C proved to produce ample amounts of precipitates, which are typically 60 Å in diameter after one hour of annealing, but show sizes of up to 400 Å after two hours. Attempts to identify the particles by diffraction patterns have not yet been successful. It is hoped to heat treat some specimens in the electron microscope by means of a newly acquired device and thereby to gain more information about growth, shape, and character of the particles.

B. Dislocation Contrast

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

The contrast of screw dislocation images in electron micrographs has been computed employing the displacement field in a plate (D_p). Both the kinematic and the dynamic theories of electron diffraction have been used. Parameters were: the thickness T of the foil, the distance ξ of the dislocation from the surface, and the diffraction conditions. A thorough discussion of the results is forthcoming. Some interesting points may be mentioned: results in the kinematical case are similar for the displacement field of infinite space (D_∞) (results of other authors) and for D_p (present results). However, the image of the dislocation shifts towards the position y_{GO} predicted by geometrical optics if D_p is employed. If the image consists of two lines, these are left and right of y_{GO} with D_p, whereas D_∞ predicts them to be both on one side. D_p yields double images already for first order reflections as opposed to D_∞. Results of the kinematic and the dynamic calculations (both performed with D_p) are generally somewhat different. The striking feature is, however, that both methods yield very similar results if care is taken that the relations between T and ξ and the periodicity length t_o' of the "Pendellösung" of electron waves are the same in both cases, i.e., if $\frac{T}{t_o'} = n = \text{const.}$ and $\xi/t_o' = m = \text{const.}$ in both cases. This means that contrast profiles predicted by kinematic theory are verified in foils of somewhat different thickness T and for dislocations in somewhat different depths ξ, both T and ξ being usually not known for any particular dislocation micrograph. We suggest that this is the reason why the simple kinematic theory quite often yields results which check out surprisingly well.

C. Elasticity Theory of Dislocations in a Semi-Infinite Region
Dr. W. B. Pfeiffer, Department of Mechanical Engineering

The investigation of displacement functions mentioned in the last reports has been concluded. Simultaneous plots of displacement functions in infinite space and in a semi-infinite region computed for various parameters give a vivid impression of the influence of the surface. A manuscript entitled "Verschiebungsprofile von Stufenversetzungen in einem Halbraum" will be submitted shortly for publication in the "Zeitschrift für Naturforschung."

D. The Effect of Controlled Solute Atom Addition and Temperature Upon Damping and Yield Phenomena in Magnesium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

The memory effect discussed in the last semi-annual report has been observed to increase with increasing impurity content, temperature, and time. This effect is not observed in the crystal doped with 0.5 atomic percent Al, the maximum impurity level studied, as this crystal exhibits linear elasticity up to the macroscopic yield limit. Barriers formed by impurity migration to dislocations appear to be responsible for the effect. Since the effect is observed only on that portion of the unidirectional damping loop where it was previously established by anneal, the Granato-Lücke concept (J. App. Phys., 27, (1956)) cannot be used as a model for describing the damping loops. The PhD dissertation by Mr. David Hartman describing the above effect and the phenomena reported in the last Semi-Annual Report should be complete within two months, with publication following shortly thereafter.

E. Dislocation Damping in Copper Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

The results of this study, "Microstrain and Low Frequency Hysteretic Dislocation Damping in Copper Single Crystals", by D. M. Barnett and J. M. Roberts, have been accepted for publication in Trans. AIME.

F. Microcreep in Molybdenum Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

Since the last Semi-Annual Report the necessary modification of existing creep apparatus has been performed to permit microcreep studies of 1/8" diameter molybdenum single crystals loaded in tension. Use of this capacitance type extensometer allows study of creep rates in the range down to 10^{-4} sec^{-1}. Preliminary testing of one crystal, primarily at room temperature, has been

completed. Tests are now in progress on a second crystal covering a temperature range of 200° to 300°K. Notable points found so far in the small strain region are that microcreep following incremental loading seems to be composed of two parts. The initial creep rate is transient having a rate which decreases exponentially with strain. Following this usually brief transient period the creep assumes a constant rate. This constant rate is a function of the applied stress, temperature, and prior straining of the crystal. The steady-creep rate has been found to be very strongly temperature dependent, indicating a rather large activation energy. The activation volume of this constant creep rate process appears to be a function of temperature but not of prior strain. Analysis of the transient portion of the creep data is in progress.

During straining of the crystal between creep tests, an attempt has been made to observe microstrain hysteresis loops in order to correlate microcreep and microstrain studies. This has met with only limited success. It may prove necessary to change the specimen gripping arrangement to achieve even better axiality of loading necessary for reliable results from the cyclic loading tests.

G. Phonon-Dislocation Interactions

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

Results reported in the last Status Report were collected in a manuscript forwarded to NASA. A short paper on the subject is being prepared for publication.

H. Electrical Resistivity of Deformed Molybdenum Single Crystals

Dr. F. R. Brotzen, Department of Mechanical Engineering

Increase in resistivity versus deformation is linear for a deformation temperature of 195°K. Tests for a deformation temperature of 273°K are not complete, but the initial results indicate a linear relationship. Evaluation of the relative magnitude of resistivity due to vacancies and dislocations when deformed at 195°K and 273°K has begun. Results are insufficient for discussion at this time.

I. Direct Observation of Lattice Defects in Molybdenum

Drs. W. B. Pfeiffer and F. R. Brotzen, Department of Mechanical Engineering

The preparations for an electron transmission study of molybdenum single crystals deformed in shear are in the final stages. A used spark cutter has been adopted to cutting slices of the

deformed crystal. The surface damage as evidenced by Laue asterism seems to be less when this method is employed than after using a wire slicer employing an abrasive paste. An acid jet polishing apparatus for preparing thin foils has been constructed.

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

Equipment for testing in shear and obtaining results for strains below 20% should be ready soon. Evaluation of the effect of impurities on the stress-strain relationship and activation volume in shear and tension will start after receiving this equipment

K. Ultrasonic Attenuation of LiF Crystals Between 2^{o} and $300^{o}K$
Drs. M. Yabe and J. M. Roberts, Department of Mechanical Engineering

The construction and calibration of the equipment were done for the internal friction measurement of γ-irradiated LiF crystals at very low temperatures.

The liquid He cryostat for irradiation experiments was completed and its performance tested over a long period. As some defects were noted, efforts were made for the improvement of the cryostat. The performance of the cryostat is still inadequate but it is hoped that the troubles will soon be removed.

Theoretical consideration has been given to an acoustical composite system, which includes a quartz transducer, a very thin (i.e., thickness much smaller than the wave length used) viscoelastic adhesive layer, and a large sample. This study centers about the accuracy of internal-friction measurement by an ultrasonic pulse technique in the frequency range between 5 Mc to 300 Mc. The study will result in an improvement of the technique.

Further consideration has been given to internal friction at very low temperature in alkali-halides containing point defects of low symmetry. Such point defects would be expected in the experiments planned presently. The point defects should give rise to internal friction by means of thermal motion of the ions surrounding the point defects, even at very low temperature (i.e., near liquid He temperature)

A paper,"Low Temperature Annealing of the Ultrasonic Attenuation in Prestrained LiF after Co^{60} Gamma Irradiation at Liquid Nitrogen Temperature" was sent to J. Phys. Chem. Solids. It was returned for editorial changes.

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

Since the last Semi-Annual Report, progress has been made in the theoretical investigation of fracture along welded bimaterial interfaces. Even though stresses around a static crack along a bimaterial interface show a sharp oscillatory character, stresses around a propagating crack are non-oscillatory. There exists a single velocity at which a fracture may propagate along an interface. The velocity is determined by the ratios of various elastic constants of the two media. The limiting velocity of such fractures is the lower of the two Rayleigh wave velocities. Surprisingly there is no relation between the fracture velocity and the Stoneley wave velocity.

Further work is being continued on fractures in bimaterial media and anistropic media.

Publication since May 1964:

L. Mansinha, "The Propagating Fracture of Constant Shape", Accepted for publication by the Journal of Mechanics and Physics of Solids, London.

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

This work has been completed and a manuscript is being prepared for publication. The results indicate that the metastable β phase can be stabilized by low-temperature annealing.

N. 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. Accessories for the existing X-ray equipment required to perform the necessary diffuse scattering experiments are being assembled.

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. This effect has been attributed to either the destruction of SRO, or changes in the number of carriers produced by dislocations. A series of experiments are in progress to differentiate between these two explanations. (One doctoral candidate).

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

The resonance frequency in a disordered Cu-Au sample is measured at constant temperature. As ordering occurs, the natural frequency changes because of changing elastic constants. Tests completed show that short-range order causes a rise in the elastic constant but long-range-order has the opposite effect.

Electrical resistivity measurements are being carried out to correlate resonance with resistivity results.

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

Recent results in another laboratory indicate that the plastic properties of Ge are strongly dependent on whether the material is either 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.

Because of the temporary absence of Dr. J. M.Roberts, Department of Mechanical Engineering, who is spending his sabbatical leave in Professor J. Friedel's Institute in Orsay, France, the following two projects remained dormant during the last six months:

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

Microcreep in Single Crystals of Magnesium

III. Chemistry of Solids

A. Order-Disorder Analysis of Lattice Systems

Dr. Z. W. Salsburg, Department of Chemistry

1. Monte Carlo Calculations for Lattice Systems

The study of the thermodynamic behavior of "hard hexagon" lattice-gas models by Monte Carlo computer calculations has continued along the lines discussed in the last report. The importance of this model is contained in its apparent phase transition - a transition which could play an important part in elucidating the role of repulsive forces in solid-liquid transitions. Further calculations for larger lattices (i.e. 480 sites) have been carried out on the Rice Computer with inconclusive results. While the model displays a definite transition we have not been able to determine if it is a first-order transition or not.

Since we have exhausted the capacity of the Rice Computer (as well as all other computers available to us in this area) we have first of all reformulated the computer program to more effectively sample configurations in the transition region and are recoding it for the CDC 6600 computer. The Livermore Radiation Laboratory, which has had a continual interest in this problem, has kindly extended us an invitation to use their CDC 6600, the only one available at this time. The program is currently being checked and we plan to continue our studies before January 1, 1965.

2. Second Largest Eigenvalue of Large Probability Transition Matrices

The statistical mechanical investigations on the triangular lattice gas model involve the averaging in the Grand Canonical Ensemble of properties of states generated by a Markov chain is formally equivalent to the convergence of the vector iterate of a stochastic matrix representing the transition probabilities between the states of the system. Since the probability transition matrix for a given system is not uniquely defined, the selection of the optimum matrix (optimum with respect to speed of convergence) is of some interest. To a first approximation, the nth vector-iterate of a probability transition matrix converges to the first eigenvector as the nth power of the second largest eigenvalue of the matrix.

The second largest eigenvalues of a series of 512x512 probability transition matrices were calculated by a computer technique involving iteration of the matrix by a vector orthogonal to the first eigenvector. Within the series of matrices considered, for all values of the temperature parameter, minimum values of λ_2 were obtained for matrices in which $p_{ii} = 0$, corresponding to a Markov chain selected so that no state immediately succeeds itself.

These studies are now being applied to the various Monte Carlo schemes under consideration to determine an optimum computer program.

B. Thermal Emittance Measurements of Nickel As A Function of Oxide Thickness

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

Work has continued on measurement of the total hemispherical thermal emittance of nickel as a function of oxide thickness. Additional data have been obtained at lower (300-400°C) and higher (900-1200°C) temperatures. A minimum in the "emittance vs. temperature curve" has been observed in the vicinity of the Curie temperature for both the bare and oxidized nickel.

Thermal emittance measurements are being extended to single crystals of nickel to determine the effect of crystal orientation and oxide structure. Oriented single crystal samples 3" long x 1/6 wide x .010" thick have been prepared with good X-ray back reflection Laue photographs of the (100) and (110) planes. The single crystal specimens were prepared by spark cutting an 8" long x 1/2" diameter oriented single crystal purchased from Research Crystal, Inc., in Richmond, Virginia. The spark cut samples were mechanically thinned and chemically polished to obtain a thin, strain-free, bright surface. Additional single crystal specimens, including the three principal faces - (100), (110) and (111) - have been purchased from Semi-Elements, Inc. in Saxonburg, Pennsylvania.

Since strain-free single crystals below 10 mils in thickness are difficult to obtain, it was necessary to modify the equipment to handle the thicker samples. A larger power supply unit was purchased along with a quartz microbalance to measure the small amount of oxide on the heavier samples.

C. High-Temperature Interactions Between Gases and Condensed Phases

Dr. J. L. Margrave, Department of Chemistry

The Bendix mass spectrometer and the magnetic mass spectrometer are being utilized for studies of a variety of high temperature gas-solid interactions. In addition, three microbalances are being operated to provide information about vaporization and sublimation processes from Knudsen and Langmuir weight-loss measurements.

The species over the systems CrF_2 and $SrCl_2$ have been established mass spectrometrically, and the thermodynamic properties of the dihalide monomers were derived. Mass-spectrometric measurements on the vapor pressure of nickel are consistent with the older data

quoted by Stull and Sinke* and do not support the suggestion of Nesemeyanov** that the vapor pressure should be higher by a factor of 10^4. The reaction between CrF_2 and Cr has been utilized to produce the monofluoride, CrF(g), and it has been thermodynamically characterized.

Vapor pressure work using the Knudsen effusion technique in conjunction with the vacuum microbalance in the low-temperature phase (0-300°C) has concerned itself with the measurement of the vapor pressures of several organic compounds in an attempt to correlate thermodynamic properties with structural features. The compounds studied have been pairs of methyl-substituted organic molecules and the current results are summarized in Table I.

The globular nature of the dimethylbenzo (a) anthracenes is clearly shown by comparing their ΔH_{sub} and ΔS_{sub} with those of anthracene ($\Delta H_{sub} \approx 23.5$ kcal.mole^{-1}; $\Delta S_{sub} \approx 40$ ev) and napthalene ($\Delta H_{sub} \approx 17.0$ kcal.mole^{-1}; $\Delta S_{sub} \approx 40$ ev). The ΔH_{sub} and ΔS_{sub} values for the 3, 9-compound are higher than these for the 1, 12-compound, showing the effect of the protruding methyl groups in the former compound. A value of $\Delta H_{sub} = 34.4$ kcal.mole^{-1} is obtained for these compounds using Bondi's molecular increment system.

ΔH_{sub} and ΔS_{sub} for the 2, 4, 5, 7-compound are less than for the 3, 4, 5, 6-compound, suggesting that the packing in the former crystal is less efficient, or that there is an activation energy and/or entropy involved in sublimation of the latter compound. A value of $\Delta H_{sub} = 31.7$ kcal. mole is obtained for these compounds using Bondi's system of molecular structive increments.

High temperature studies on $SrCl_2$ single crystals have been made with the Ainsworth recording microbalance. The results indicate ΔH^o_{298} for $SrCl_2$ sublimation = 78.6 ± 3.5 kcal mole^{-1} and $SrCl_2$ monomer has been established as the vapor species. There is evidence here, as in the case of other alkaline earth difluorides, that α, the Langmuir coefficient, is in the range 0.2 - 0.5. A manuscript reporting the work is in preparation and will be submitted to the Journal of Physical Chemistry soon.

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* D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements", Advances in Chemistry Series, No. 18, (1956).

** An N. Nesmeyanov, "Vapor Pressure of the Elements," (English Translation), Academic Press, pp. 390-397 (1963).

Molecular beam research has been relatively inactive because of the unavailability of personnel from June 1 until late August when Dr. C. H. Williams arrived from Brown University. Now plans and equipment design modifications are in progress for molecular beam experiments. Velocity selector and detector designs are among the current interests.

TABLE

Vapor Pressures of Selected Molecules

By Knudsen Effusion Studies

Compound	Temp.Range °C	ΔH_{sub} kcal $mole^{-1}$	ΔS_{sub} Cal. $mole^{-1}deg^{-1}$	ΔF_{sub} kcal. $mole^{-1}$ at °K
1,12 dimethyl benzo(a)anthracene	88 - 115	23.4 ± 1.4	35.3 ± 1.5	10.2 (373°)
3,9 dimethyl benzo(a)anthracene	107 - 141	27.0 + 0.9	41.1 + 0.9	11.7 (373°)
*3,4,5,6-tetramethyl phenanthrene	52 - 68	31.8 ± 4	67.1 ± 1.2	8.8 (343°)
2,4,5,7 tetra methylphenanthrene	55 - 96	28.0 ± 0.4	55.4 ± 0.4	9.0 (343°)

*Determination still in progress: final values for ΔH and ΔS could be lower than this by 1 kcal.mole (ΔH) and 2 cal.deg.$^{-1}$ mole^{-1} (ΔS).

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

The crystal structure of the diazonium salt p-diazonio sulfonate has been determined by X-Ray diffraction techniques. The ring system was found to be quinoid in character. The diazonium group is linear with a C-N distance of 1.39 Å and an N=N distance of 1.14 Å.

Continued work on carbanion structures has led to a correct trial structure for the compound potassium p-nitrophenyldicyanomethide. The refinement of this structure is presently in the final stages. Structural investigations of potassium and ammonium 1,1,2,6,7,7 hexacyanoheptatrienide are also in progress. These structures appear

to be isomorphous, crystallizing in the space group $P2_1/c$. A structural refinement based on the method of isomorphous replacement should lead to an unambiguous solution of both structures.

We have also prepared crystals of the compound ammonium trinitromethide in order to study the structure of a carbanion containing adjacent groups other than the cyano group. Complete X-ray data has been collected from these crystals and a trial structure is being sought from two and three dimensional Patterson syntheses. No meaningful results have as yet been obtained.

Other nonionic structures at present under investigation are of the compounds cis-2-4-butylene episulfone and tetracyanoethylene oxide.

Past work has led to recent publications:

Charles Bugg, Jimmy Lawson and Ronald L. Sass, "The Crystal Symmetry of Several Diazonium Salts," Acta Cryst., 17, 767, (1964)

Charles Bugg, Robert Desiderato and Ronald L. Sass, "An X-ray Diffraction Study of Nonplanar Carbanion Structures," J. Am. Chem. Soc., 86, 3157, (1964).

E. 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 been redesigned to give more sensitivity and better control over the catalytic reactions at the solid surface. Development of this apparatus is continuing. The reaction now under study is the oxidation of CO on metal oxides.

The new apparatus and new direction of this study are aimed at the following objectives:

1. Comparison of the rates of chemisorption and catalytic reaction on powders and on single crystals of the same material. The new apparatus is designed with sufficient sensitivity to measure these rates on single crystals.

2. This comparison is being studied by making radiations induced perturbations of the Fermi level. An attempt is being made to separate these perturbations according to the following mechanisms:

   a. Transmutation (or chemically induced) impurity doping,

b. Radiation induced dislocations and lattice damage, and

c. Electronic excitations - induced by various monochromatic ultraviolet sources.

3. The effect of these perturbations on electrical measurements of bulk conductivity and Seebeck Coefficient is to be compared with the rates of chemisorption and catalysis.

A series of measurements in underway on the response to radiation of MgO doped chemically with different concentrations of Fe impurities and with varying surface concentrations of H_2O and CO_2 using the H_2-D_2 exchange reaction. This is to verify the catalytic mechanism effects predicted by some of the results of Lunsford in his earlier work at Rice and his subsequent research at NASA.

The paper on H_2 adsorption on Cds films containing S^{35} has been accepted for publication in the Journal of Catalysis.

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

Work just completed on the application of the two-dimensional equation of state to physically adsorbed hydrocarbons on charcoal is being presented at the National Meeting of the American Institute of Chemical Engineers to be held in Houston in February 1965. This study is continuing.

G. Chemisorption of Solids
Dr. H. A. Deans, Department of Chemical Engineering

The study of chemisorption on a solid support, employing perturbation chromatographic techniques, is continuing. Apparatus has been constructed to encompass a wide range of surface coverages and temperatures. The system chosen for study is carbon monoxide-helium chemisorbed on a zinc oxide-copper oside catalyst. The available temperature range is 75° to 800°F while the pressure range is 1 atm. to 8 atm. Initial measurements are being carried out.

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

Present work involves the application of the Kihara potential for non-spherical, non-polar molecules to study hydrate-formation conditions for temperatures in excess of 32°F and pressures up to 4000 atm. Computer calculation based on the mathematical formulations of Dr. I. Nagata, a postdoctoral fellow, are presently being carried out.

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

This project has two objectives:

A. To develop and apply the chromatographic theory to study adsorption in gas-solid systems. Since the last Semi-Annual Report we have succeeded in converting the equipment to study both radioactive and non-radioactive perturbations, checked adsorption isotherms for methane on activated charcoal obtained by a classical material balance method, and developed a technique of obtaining the volume of adsorbed gases.

B. To study gas-liquid to gas-solid phase transitions in multi-component systems by gas chromatography. Dr. Anand, a post-doctoral fellow, has essentially completed rebuilding the equipment and should be making experimental runs within a month on the methane-propane-n-decane system at temperatures below -21°F, the freezing point of n-decane.

Date: 3 December 1964

Signed: Franz R. Brotzen

Franz R. Brotzen

Dean of Engineering