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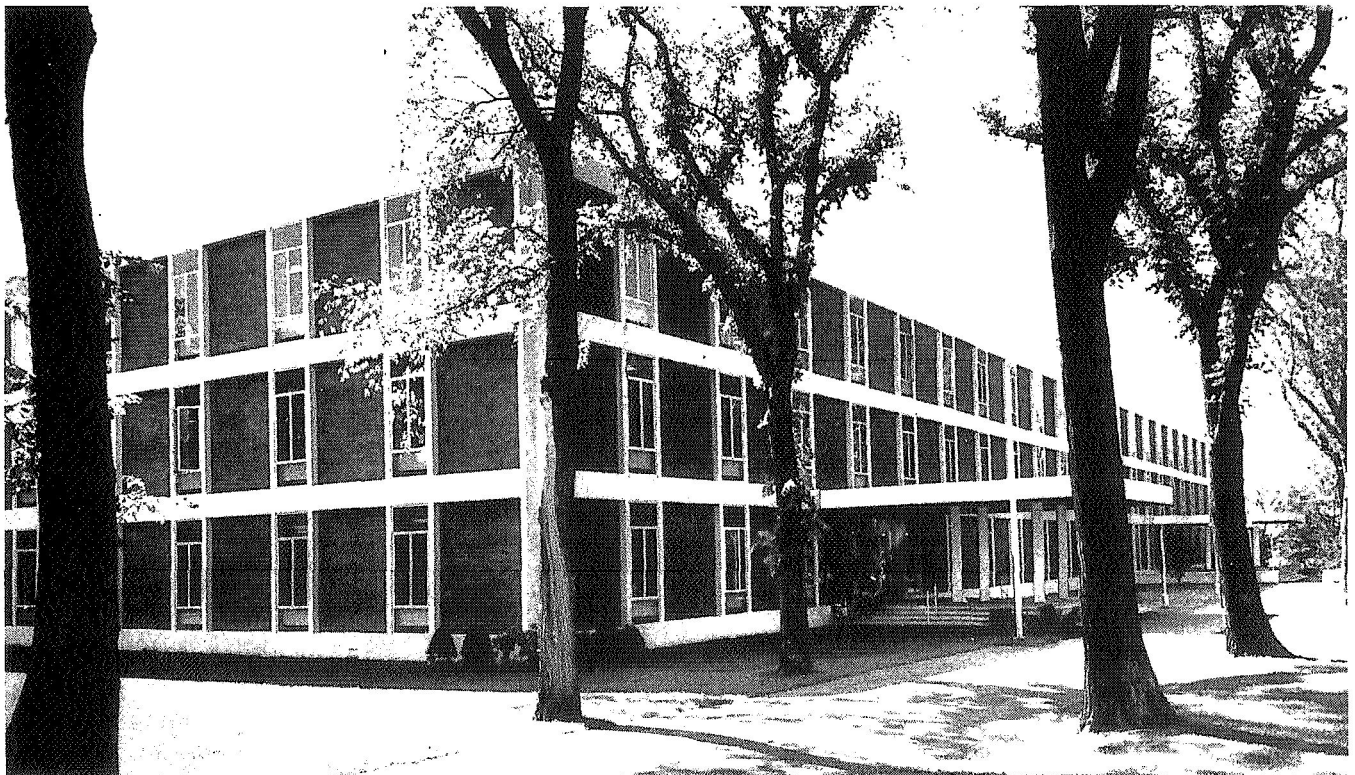
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Materials Research

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SEMI-ANNUAL PROGRESS REPORT
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

GRANT NO.
~~NGL-33-018-003~~

~~/~~ Rensselaer Polytechnic Institute
Troy, New York

September 1969

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Rensselaer Polytechnic Institute
Troy, New York

Semi-Annual Progress Report
National Aeronautics and Space Administration Grant NGL-33-018-003
March 1, 1969 to August 31, 1969

INTRODUCTION

The summer of 1969 again saw industry benefiting from the spin-off from the NASA supported Materials Research Program at Rensselaer Polytechnic Institute. During the summer four courses directed toward industrial personnel were given by the Materials Research Center staff. NASA support in these areas enabled Rensselaer to develop areas of expertise and the facilities which were instrumental in enabling these programs to be carried out.

The programs were "Metallurgical Applications of Electron Microscopy," coordinated by Professors G. S. Ansell and G. Judd; "Principles of Color Technology," coordinated by Professor F. W. Billmeyer, Jr.; "Color Technology for Management," coordinated by Professor F. W. Billmeyer, Jr.; and "Advanced Color Measurement," coordinated by Professor F. W. Billmeyer, Jr.

During the report period, Dr. J. D. Mackenzie left the employ of the Institute. His research endeavors are being taken over by other Materials Research Center staff members. The University is actively seeking additional staff in the glass-ceramic research areas.

This seventeenth semi-annual summary report follows the same format as the previous report with the emphasis on function rather than on discipline. It is again divided into five sections, each preceded by a semi-technical introduction which gives a broad picture of the research going on in that particular area. These introductions are followed by more technical write-ups of the research being conducted. The five areas are:

Structural Characterization, Solid State Reactions and Phase Transformations,
Mechanical Properties and Strengthening Mechanisms, Electronic and Thermal
Properties, and Environment-Sensitive Behavior.

STRUCTURAL CHARACTERIZATION

This period has seen a number of changes of emphasis and direction in our studies of the structural characterization and synthesis of materials. Among others, it now appears that our interest in synthesis is secondary to that in characterization to the extent that it is hardly appropriate to include the term synthesis in the title of this section. That is, in this group we tend to synthesize materials as required to further our characterization needs. An example is the structural characterization of linear aliphatic polyesters, the concluding report of which is included in this section: the polyesters were synthesized as required to provide the materials for this study.

Other projects included in this section of previous semi-annual reports have likewise been terminated, either temporarily as a result of personnel changes (primarily as graduate assistants receive their degrees) or permanently. Such projects include our work on amorphous films, selenium-based glasses, the deposition of pyrolytic carbon, dispersion in gel permeation chromatography, and polymerization kinetics.

In other areas, our work has taken on new directions which give promise of results of great interest in the coming period. For example, interest in our studies of low-temperature specific heats of polymers has spread to several other groups, with the result that this report includes contributions describing studies, or plans for study, of low-temperature NMR, ESR, and anelastic relaxation phenomena in similar polymer systems.

In another area, our efforts towards the accurate calibration of angular-dependence and low-angle light scattering equipment have largely

been completed, and of a number of systems of biological interest studied in preliminary fashion (as described previously), one has been selected for in-depth study using these characterization tools.

BORON FILAMENT DEPOSITION

Senior Investigator:

R. J. Diefendorf

The most widely-used process for boron filament production is hydrogen reduction of boron trichloride to vapor-deposit boron on a hot tungsten-wire substrate. Tungsten is used as a substrate since it is the only conductive refractory material that is readily available in a fine-diameter wire (.0005"). However, tungsten has some disadvantages as a substrate for high-strength, high-modulus, low-weight boron filament. It has a high density, is not available in large quantities, and is costly.

These disadvantages can be overcome by substituting carbon as a substrate material. Carbon is available in the monofilament form with low density (1/12 that of tungsten), good electrical conductivity, and a smooth surface. It is a raw material readily available in large quantities, and, most important, it is low in cost.

Under continuous deposition conditions, considerable difficulty has been encountered in producing boron filament on a carbon substrate. This has been found to be due to elongations during the deposition process. Static deposition runs in a vertical reactor have shown that elongations of 3 - 6 per cent are common during deposition on both carbon and tungsten substrates. An elongation of this magnitude far surpasses the breaking strain of the carbon monofilament. Thus, it is found that the substrate breaks apart during deposition producing a poor filament. This elongation is also above the breaking strain of tungsten, but at deposition temperature, tungsten is ductile and will absorb the increase whereas carbon remains brittle.

Elongation experiments as a function of time are being performed on a static reactor to determine statistically the optimum conditions for deposition of boron on carbon monofilament. The variables under statistical treatment are monofilament diameter, tension on the filament, gas composition, flow rate of gas in reactor, and temperature.

In addition, optical microscopy, the microprobe, and microhardness testing are being used to determine bonding of the boron to the carbon, and to determine the extent of diffusion of boron into carbon in the formation of a boron carbide core.

SOLID STATE AND PHASE STUDIES OF INORGANIC MATERIALS

Senior Investigator:

H. Wiedemeier

The objective of this work is continued studies of the solid state and structural properties of inorganic materials. Such investigations provide basic information for the successful preparation of materials with predetermined properties.

For many solid state investigations it is highly desirable to have available single crystals of specific dimensions. At present the vapor-transport technique represents a most suitable method for the synthesis of single crystals of high purity and crystalline perfection. The physical and structural properties of the vapor-grown crystals are affected by the experimental parameters of the transport process, in particular by the mode of mass transport. This was studied on the multi-component multi-reaction system MnS-MnSe-iodine.

Under otherwise constant experimental conditions (temperature gradient, tube dimensions, and amount of starting materials) stoichiometric mixtures of high-purity elements Mn, S, and Se in a ratio 1 Mn: 0.5 S: 0.5 Se were transported with iodine. The linear dependence of the transport rate on the iodine concentration indicated that the transport process was predominantly by convection. A quantitative confirmation of this conclusion was obtained by plotting the transport rate in terms of flux ($\text{moles/cm}^2 \cdot \text{sec}$) versus the iodine pressure in atm. The experimental plots are compared to computed transport rates for the simpler system ZnS-iodine based on diffusion theory. The results show that the experimental rates are considerably higher than predicted for a diffusion-controlled process. This demonstrates that in the MnS-MnSe and probably in related systems mass transport is predominantly by convection in a pressure range from about 1 - 15 atm. The transport product in this investigation was a solid solution of a high degree of crystallinity.

An important observation in this series of studies was the change in size and morphology of the deposited alloy single crystals as a function of iodine pressure. At lower total pressures (onset of the diffusion range) the crystals are large and well-defined and the formation of platelets seems to predominate. At medium pressures the crystals are still well-defined but they are smaller and polynucleation starts to occur. At high pressures microcrystalline products are obtained. These results are useful in developing a better understanding of the complex phenomena of nucleation of crystalline materials on amorphous substrates. It will be the purpose of systematic studies to gain more information concerning the parameters that control crystal growth and growth morphology.

ELECTRON SPIN RESONANCE

Senior Investigator:

A. C. Greene

Studies of the energetics of interstitial molecule formation in irradiated alkali halides have been continued with emphasis on the behavior of Cl_2 in NaCl . The model employed consists of a neutral Cl_2 molecule occupying adjacent interstitial sites and oriented along a $[100]$ direction. The formation of the molecule is viewed as the coupling of two H-center complexes (interstitial atom configurations) to yield the resulting molecule. The energies associated with this defect system in an otherwise perfect lattice have been obtained by minimization of the strain, polarization, and molecular interaction energies. The elastic strain energy and ion displacements were calculated using a point ion model with provisions for relaxation of 80 neighboring ions surrounding the defect center. The contribution of the polarization of neighboring ions to the total energy was calculated on the basis of 48 neighboring ions, the reduction in crystal size being necessary due to the increased complexity of the calculations. The following energies have been found: elastic strain energy, 5.98 eV; polarization energy, -0.55 eV; molecular bond energy, -2.48 eV. Thus, the energy of the interstitial complex is 3.0 eV above that of the perfect lattice. Comparing this energy with that calculated for an isolated H-center relative to the perfect lattice (about 2.23 eV), the binding energy of the molecule relative to two isolated H-centers is found to be about 1.5 eV. This latter energy is significant since it supports the view that the interstitial molecule is stable near room temperature, whereas

experiments on H-center kinetics and decay show a rapid thermal annealing process at much lower temperatures, in the vicinity of 60 - 70K.

Further calculations of the properties of the interstitial complex are being conducted and will be continued. Of primary interest is the study of the thermal annealing properties of the interstitial molecule at relatively high temperatures, in the range from 500K to 600K. Various experiments have shown that states with considerable lattice strain, ascribed to the presence of interstitial configurations, are extremely stable below this temperature range. A detailed study will be made on the possible processes by which the interstitial complexes recombine with vacancy configurations to restore the lattice to the "perfect" state.

Thermal annealing measurements have been completed on BaS powder samples which are optically active under applied stress. F-center concentrations as high as 5×10^{17} per cc have been obtained by successive grinding of the powder followed by exposure to ultra-violet irradiation at room temperature. The annealing characteristics of the F-center concentrations appear to be complex and are currently being analyzed in detail. As the temperature is raised from 20°C the observed F-concentration increases slightly, then decreases rather slowly at temperatures near 100°C for the annealing cycle employed. From about 100°C to 170°C the annealing process is approximately second order in kinetics while at higher temperatures, to about 300°C; first-order kinetics seem to be dominant. Parallel experiments using γ -irradiation rather than ultraviolet are also being conducted. The dominant paramagnetic centers produced under γ -irradiation are different in

both spectral characteristics and thermal stability from the F-center.

NUCLEAR MAGNETIC RESONANCE

Senior Investigator:

P. A. Casabella

The study of the deformability of the ions in solid alkali halides under stress is continuing. Previously, good agreement had been obtained between model calculations and experiments performed in this laboratory on NaCl and NaBr. However, the analysis of experiments on KCl, NaF, and KBr, which is now nearly complete, shows that the previous agreement was partly fortuitous. It now appears that the model works well for positive ions but poorly for negative ions. This is because the positive ions are smaller than the negative ions. It is very difficult to take into account accurately overlap with neighboring ions and its effect on ionic deformation for the large negative ions. In addition, all calculations are based on free-ion wave functions, and these are a much better approximation for the small positive ions than for the negative ions in the solid.

However, this study has provided accurate experimental data which will be useful in analyzing other experiments on alkali halides, particularly those concerned with studies of defects and radiation damage. It is expected that qualitative results will be available for the next semi-annual report.

Since the last report a pulsed nuclear magnetic resonance system has been assembled to measure spin-lattice relaxation times in polymers. The system is now completed and has been tested in several experiments. In the next six months the study of polymers at low temperatures will be undertaken with this new apparatus.

ANELASTIC RELAXATION

Senior Investigator:

R. K. MacCrone

Mechanical loss measurements have been made on two polymers, poly(methyl methacrylate) and polyethylene, at low temperatures. Poly(methyl methacrylate) shows two small relaxation peaks at low temperatures, $< 10\text{K}$, while polyethylene shows three relaxation peaks below 50K . The explanation of these relaxations is based upon peaks in the phonon-distribution curves of amorphous materials. These peaks have been best demonstrated by theoretical calculations and low-temperature calorimetry. A theoretical analysis of the expected mechanical relaxation strengths has been made and the relaxation strength as a function of temperature derived. Good agreement between theory and experiment has been obtained. The theoretical analysis of the relaxation time describing the dynamic response is much less certain, although qualitative agreement has been obtained. The experimental measurements and theoretical development continue.

LOW TEMPERATURE THERMODYNAMIC STUDIES

Senior Investigator:

G. L. Salinger

Measurements of the thermal conductivity of polymers have been halted temporarily until a better understanding of their specific heat is obtained. As previously reported, the specific heat of polymers at low temperatures can be described as a Debye T^3 contribution plus an excess specific heat. So far we have analyzed this excess specific heat in terms of independent oscillators which we assume to be pendant groups or chain

ends oscillating near packing voids. These oscillators enter into the calculations for the thermal conductivity as an additional scattering mechanism and lower the thermal conductivity. This may explain the deviation of the experimental measurements of the thermal conductivity from the theoretical predictions below 1K.

On the other hand, the density-of-states curve for the acoustic modes in polymers may include dispersion even at these low temperatures. This would also affect the heat capacity term in the thermal conductivity calculations. Lower temperature heat capacity and thermal conductivity measurements will be needed to decide between these alternatives. The localized modes which we obtain from our specific heat measurements have been used to fit the thermal conductivity of poly(methyl methacrylate) from 2 - 300K to within 10 per cent.

In the past six months the specific heat of poly(methyl methacrylate) and polystyrene were remeasured. It was discovered that the use of helium exchange gas to cool the sample gave rise to spurious results at low temperatures. Furthermore the method of applying heat to the sample was changed to avoid effects of power transients. The elimination of these two effects has considerably improved the low temperature data. A heat switch has been developed so that data can be taken continuously from 0.4 to 4.2K. In addition, the data analysis has been much improved and shortened by the use of computer techniques. Programs have been developed to calibrate carbon resistors and to calculate the heat capacity from the data. We also have programs to determine the frequencies and strengths of the independent oscillator modes. This work will lead to a Masters Thesis for R. G. Hunt.

POLYMER-SOLVENT INTERACTIONS

Senior Investigator:

S. S. Sternstein

The constant-volume cell described previously is being modified to allow interaction studies of polymers and liquids at high pressure. This will enable us to determine what effect, if any, solvent activity has on the diffusion and equilibrium processes, at constant temperature. Theoretical work is continuing on the development of a suitable model for the thermodynamic interaction of solvents with polymers constrained to constant density.

LOW-ANGLE LIGHT SCATTERING STUDIES

Senior Investigator:

F. W. Billmeyer, Jr.

Our low-angle light scattering photometer is being used to measure the molecular weights of various samples of DNA. The instrument is particularly well suited for this type of work in that the extrapolation to zero scattering angle inherent in the Zimm method of determining molecular weights is no longer necessary. With this instrument, one can measure the intensity of scattered light to within one degree or less of the primary beam, eliminating a major difficulty in obtaining accurate molecular weights of DNA that has been encountered by other workers.

The goal of the project is to measure and compare the molecular weights of samples of DNA taken from normal and neoplastic human tissue, in order to determine whether any real differences between corresponding samples

do exist. The first step in this project will involve the calibration of the instrument using absolute turbidity standards, such as Ludox silica sols to obtain absolute scattering intensities. Once the instrument has been calibrated, it will be used in conjunction with our conventional wide-angle photometer (previously calibrated in a like manner) to study the full range of angular scattering of the DNA samples.

At present, we are working with a sample of calf-thymus DNA, the accepted molecular weight standard for most work with DNA, in order to acquaint ourselves with the procedures involved, prior to beginning the calibration of the low-angle instrument.

This project is being undertaken in conjunction with Dr. Robert Fiel of Roswell Park Memorial Institute, who will supply all the necessary DNA samples, and will assist in other specialized aspects of the work.

THE REFRACTION CORRECTION IN LIGHT SCATTERING

Senior Investigator:

F. W. Billmeyer, Jr.

We have undertaken a rigorous and definitive study of the theoretical and experimental aspects of the refraction correction in light scattering. For the past 25 years, almost since the beginning of modern light-scattering work, there has been considerable doubt as to the nature of the refraction correction term for the case of a cylindrical scattering cell. Several theoretical interpretations support both n and n^2 correction terms, where n is the refractive index of the scattering liquid;

but to the best of our knowledge, there has never been any definitive experimental work published distinguishing unequivocally between these. We have made such an experimental study, and in agreement with our theoretical interpretation, find that n^2 is the proper refraction correction term for the case of a cylindrical scattering cell in a photometer where the phototube does not see past the edges of the primary beam.

We measured the absolute excess turbidity at 90° angle for a series of seven pure liquids of differing refractive indices whose Rayleigh Ratios are well known. These measured values were then plotted in such a way that the least-squares slope of the resulting line gave the exponent of n in the refraction correction term. For measurements done in both blue and green light, the exponent of n was $2.00 \pm .007$.

Other experiments were performed using the turbidity standard known as the Debye polystyrene, "Ludox" silica sol, and 12-tungsto-silicic acid as a standard of known molecular weight (3311.52). In each case, application of the n^2 correction led to reproduction of the assigned properties of the standard to within 0.25 per cent.

In a computational approach, we demonstrated by ray tracing that the phototube in our photometer does not see past the edges of the beam. We then proved geometrically that light scattered by particles within the scattering volume of the cell is refracted in the horizontal direction as well as in the vertical, so that there is a factor of n contributed to the refraction correction term from each dimension, the resultant factor being n^2 .

THERMODYNAMICS OF SYSTEMS OF SEMI-CRYSTALLINE POLYMERS AND SOLVENTS

Senior Investigator: F. W. Billmeyer, Jr.

Studies are proceeding upon three samples of polybutene-1 with approximate melt indices of 0.2, 0.5, and 1.2 at 190°C. This range of melt indices corresponds to number-average molecular weights of 100,000 to 300,000.

Polymer densities have been determined using a flotation technique at 30°C. Ethanol and water were used as solvents. The density of the solvent mixture was determined using standardized picnometer bottles at that exact point at which the polymer pieces just began to float.

Duplicate runs were performed for each of the three molecular weights. The average result at 30°C was $0.9066 \pm .0012 \text{ g cm}^{-3}$. No molecular weight dependence was noted. Using the calculated crystalline density from x-ray analysis of 0.95 g cm^{-3} for form I, and, that of 0.86 g cm^{-3} for the amorphous regions, obtained by Holland and Miller,¹ a value of approximately 60 per cent crystallinity was determined.

Dilatometry experiments from 30°C to 56°C were performed upon all three samples. The expansion coefficients fall between the values reported by Powers, Hoffmann, Quinn, and Weeks² which were $8.07 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$ for the amorphous and $4.51 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$ for the pure form I crystal.

This work was supported by the American Oil Foundation.

¹V. F. Holland and R. L. Miller, J. Appl. Phys., 35, 3241 (1964).

²J. Powers, J. D. Hoffmann, J. J. Weeks, and F. A. Quinn, Jr., J. Res. NBS, 69A, 335 (1965).

STRUCTURAL CHARACTERIZATION OF LINEAR ALIPHATIC POLYESTERS

Senior Investigator:

F. W. Billmeyer, Jr.

Entropies of fusion, ΔS_f , of poly(ethylene adipate), poly(ethylene suberate), and poly(ethylene sebacate) were calculated from the experimentally-determined melting points and heats of fusion presented in the last report, assuming these represented near-equilibrium quantities. The appropriate values are listed below:

Polyester	T_m °C	ΔH_f $\frac{\text{cal}}{\text{mole backbone}}$	ΔS_f $\frac{\text{cal}}{\text{mole backbone}^\circ\text{C}}$
poly(ethylene adipate)	65.0	502	1.48
poly(ethylene suberate)	75.5	527	1.51
poly(ethylene sebacate)	83.0	546	1.54

The contribution of the volume-expansion terms to the total entropy of fusion was calculated assuming that

$$\Delta S_v = \left(\frac{\partial P}{\partial T} \right)_v \Delta \bar{V}_m$$

where $\Delta \bar{V}_m$ is the appropriate volume expansion on melting and $\left(\frac{\partial P}{\partial T} \right)_v$ is the differential pressure-volume variation, evaluated in this research from compressibility measurements on the three polyesters in conjunction with the dilatometric data presented earlier. The respective conformational entropies were calculated by difference from the volume expansion entropies and the measured total entropies of fusion. The data appear below:

polyester	$\left(\frac{\partial P}{\partial T} \right)_v$ $\frac{\text{eu}}{\text{cm}^3}$	$\Delta \bar{V}_m$ $\frac{\text{cm}^3}{\text{mole backbone}}$	ΔS_v $\frac{\text{cal}}{\text{mole backbone}^\circ\text{C}}$	ΔS_c $\frac{\text{cal}}{\text{mole backbone}^\circ\text{C}}$
poly(ethylene adipate)	0.24	1.60	0.38	1.10
poly(ethylene suberate)	0.21	1.91	0.39	1.12
poly(ethylene sebacate)	0.18	2.16	0.38	1.16

We have also calculated the conformational entropies of each of the polymers statistically using a computer enumeration scheme and appropriate model chains for the polyesters. The fundamental equation in this analysis was

$$\Delta S_c = k \ell n F + (U_1/T)(G/F)$$

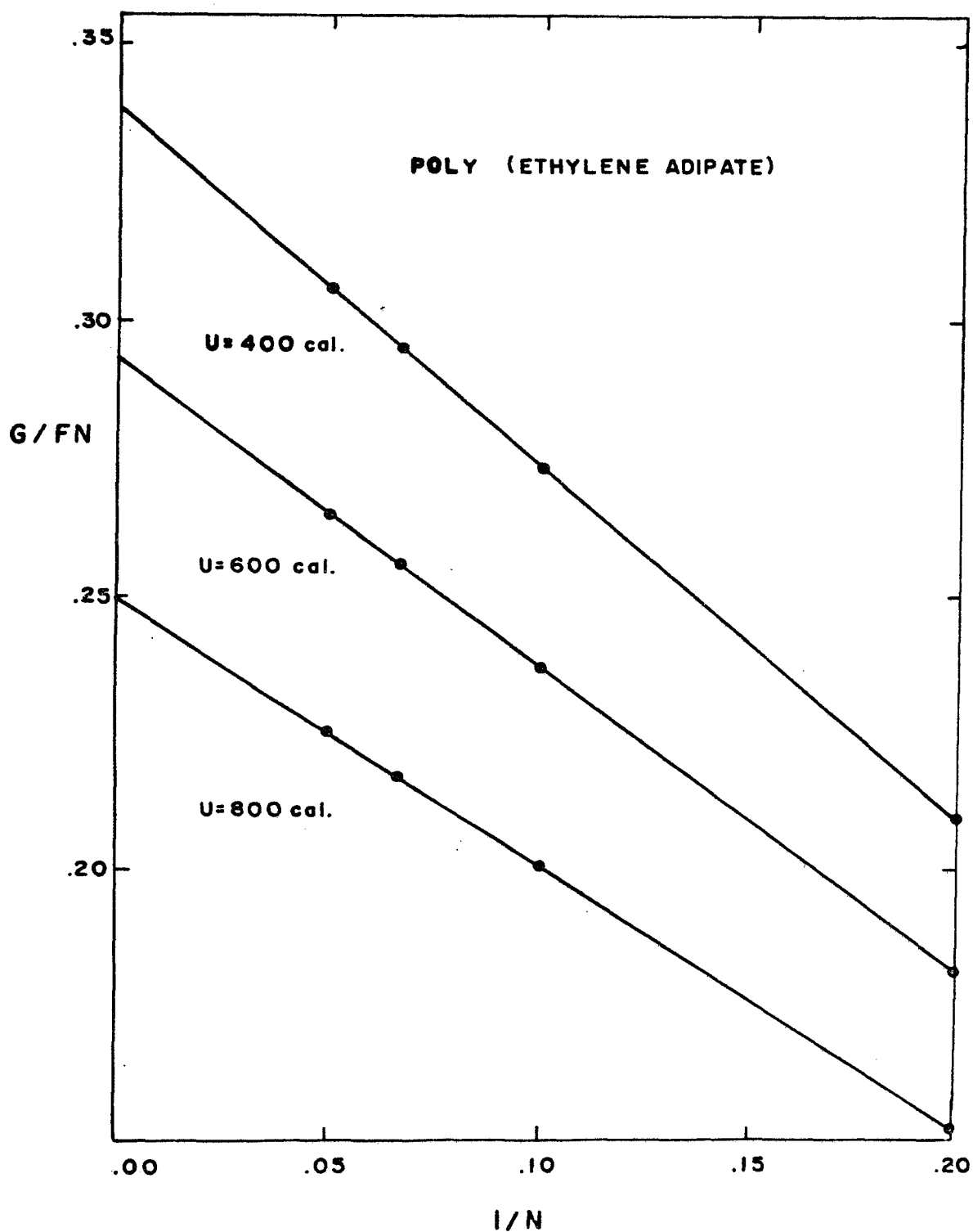
where G and F are the appropriate partition functions relating the number of possible conformation, N_j , to the "trans-gauche" energy difference, U_1 , and given as:

$$F = \sum_j N_j \exp(-jU_1/RT)$$

$$G = \sum_j j N_j \exp(-jU_1/RT)$$

These functions were evaluated for polyester chains of short length (N backbone bonds) and extrapolated both linearly and logarithmically to infinite chain length. Both extrapolations gave good straight lines; one is shown in Figure 1.

The ΔS_c values calculated for $U_1 = 400$ cal/mole (the most appropriate value for the polyester chains derived from consideration of bond rotation potential curves) were approximately 0.30 eu greater than those determined experimentally. We ascribe the difference to the presence of a high-energy twist in the $\text{-O-}\overset{\downarrow}{\text{CH}_2}\text{-}$ linkage in the crystalline polyesters which raises the entropy of the crystalline state above that appropriate for the planar zig-zag conformations assumed in the statistical evaluations. These results support a low rotational barrier (about 100 cal/mole) for the ether linkages of the polyesters while indicating that their overall chain rigidity is greater than that of polyethylene because of the included planar "trans" ester groups.



Extrapolation of G/FN to infinite chain length for poly(ethylene adipate).

FIGURE 1

Noting that the measured heats of fusion of the polyesters were substantially lower than that of polyethylene, in spite of the higher concentration of polar ester groups along the chains, we felt that dipole interactions were not making a strong contribution to the polyester heats of fusion. To confirm this assumption, we made a semi-empirical calculation of the contribution of methylene interactions alone to the polyester heats of fusion. Since the packing densities and chain conformations of the solid polyesters were almost identical to those of polyethylene, it appeared that interchain CH_2 interactions would be very similar in the two cases and proportional in total magnitude to the relative number of such groups present. The polyester heats of fusion were calculated from that of polyethylene on this assumption.

Since all four polymers show different volume changes on melting, however, interchain attractions in the melt are quite different. Thus, before comparing calculated and experimental values, we converted the experimentally-measured polyester heats of fusion to those appropriate for constant-volume melting. This was done using the Clausius-Clapeyron equation

$$\frac{dT_m^0}{dP} = T_m^0 \frac{\Delta \bar{V}_m}{\Delta H_f}.$$

A final comparison of the measured and empirically calculated heats of fusion for the three polyesters revealed that the values are quite comparable and give strong support to the assumption that methylene interactions are overwhelmingly important in determining ΔH_f for poly(ethylene adipate), poly(ethylene suberate), and poly(ethylene sebacate).

This work was facilitated through Fellowship support from the National Science Foundation.

DIFFUSION FACILITY

Senior Investigator: H. M. Gilder

We have succeeded in electrodepositing 25 micron thick layers of metallic Al^{26} onto the end faces of cylindrical, zinc single-crystal specimens. Such specimens have been annealed over the temperature range 350°C to 410°C in an attempt to determine the diffusion coefficient of Al^{26} along the principal axes of zinc. As the diffusion zone is typically of the order of a few hundred microns, the "zero time" geometry falls somewhere between that of a "Matano" Al-Zn couple and that of the more usual "thin film" specimen. As a result, Al^{26} concentration profiles that are concave upward are obtained when the logarithm of the Al^{26} specific activity is plotted against the square of the penetration distance. Radioactive standards are presently being used to determine the absolute amount of aluminum in each section. This will allow the thickness of each section, and hence the distance scale and diffusion coefficients to be determined accurately.

HARD TISSUES

X-RAY SCATTERING

Senior Investigator: J. L. Katz

Experimental studies of the elastic properties of apatites and hard tissues have been directed towards an understanding of the contribution of the mineral phase to the physical and mechanical properties of bone,

especially as can be understood in terms of a two-phase composite material.

The high pressure - ultrasonic technique has been used with continued success in systems in which porosity introduces major problems in obtaining the intrinsic modulus of a polycrystalline aggregate. In the past, this has proven to be the case with "bone mineral" (ground bone from which the organic phase has been removed by chemical treatment); previous experiments have often resulted in meaningless results. Recent measurements of the ultrasonic velocities as a function of pressure made on the "bone mineral" obtained from sea bass ribs have yielded a value for Young's modulus of 6.3×10^{11} dynes/cm² which is consistent with previous measurements made on highly-calcified systems such as enamel. Similar measurements on other hard tissues from the same and other species of fish are presently in progress; corresponding measurements are being initiated using whole human bone as well as human "bone mineral." In addition, such studies of the elastic properties of mechanical mixtures of apatites and collagen are under way.

In all of these cases the determination and identification of phases, orientation and size of particles are determined by x-ray diffraction techniques. In the case of whole human bone, small-angle x-ray scattering is being attempted with oriented specimens in order to obtain additional information about the collagen-hydroxyapatite structural relationship.

Complementary experiments are under way on the electrical conductivity of apatites, collagen, bone mineral, and suitable and appropriate mechanical mixtures of these. These experiments are also aimed at the further elucidation of the behavior of hard tissue as a composite material.

The results of several of these experiments have been utilized in a major theoretical program on the composite nature of hard tissue. Just completed is a calculation of the bounds on the elastic behavior of bone, dentin and enamel on the basis of composition. In progress is an extension of this calculation taking into account the orientation of both the collagen and hydroxyapatite as well as the particle size and shape of the hydroxyapatite.

BIOMATERIALS

Senior Investigator:

J. L. Katz

One material of long-time use in restorative dentistry is amalgam. A study of the elastic properties of dental amalgam and its alloys has just been completed using the high pressure - ultrasonic set-up. Calculations using micromechanics have been successful in explaining the elastic properties of the amalgam in terms of its composition, the elastic moduli of the individual alloys, and the calculated porosity of the sample, X-ray diffraction, electron microprobe and optical metallographic studies have been used to determine the distribution of phases in the amalgam. Continued x-ray diffraction studies have been used to determine under what conditions the Hg-Sn phase disappearance, previously discovered in several amalgam samples, can be initiated. These studies are being continued; they will be supplemented by scanning electron microscopy when the unit becomes available.

LATTICE DYNAMICS

Senior Investigator:

J. L. Katz

The thermal diffuse x-ray scattering calculations are being continued using several different models. In the case of zinc, additional refinements to the previous calculations have been introduced. The liquid He x-ray cryostat is being realigned for use with a curved-crystal monochromator. Initially planned are studies on the temperature dependence of the integrated intensities from single crystals of Cr. This will extend previous work which was limited to temperatures above that obtained using liquid nitrogen.

SOLID STATE REACTIONS AND PHASE TRANSFORMATIONS

A primary goal in the study of solid materials is the predictable attainment of specific structures together with the concomitant ability to alter the structure of solids through the use of solid state reactions and phase transformations. On this basis, the foundation of solids research, the coupling of structure to property relationships, becomes a definitive reality. The research reported in this section is directed towards this goal, the achievement of basic understandings as to the nature of a variety of solid state reactions and phase transformations for a broad grouping of solid materials, with specific interrelationships to the overall view of materials research outlined in the other report areas. While the activities in this program area are given in detail following this introductory section, the highlights of the research results during the past program period are as follows:

Several studies have been directed towards achieving an understanding of the factors controlling the kinetics of solid state phase transformations. Two areas, which have significant practical application, are precipitation from solid solution and the martensite transformation in steels. Both of these phase transformations are not clearly understood, yet are utilized as the basis for producing the majority of high-strength alloys. During this program period, the solubility of interstitial elements have been predicted for the group VIa elements, and the linkage between the kinetics of the martensite transformation and the mechanical properties of the initial phase, the austenite, have been studied. In studies of the temperature of dependence of the spontaneous polarization in Rochelle salt, it was found that the nuclear magnetic resonance method failed in the temperature range where deviations from the molecular field theory are expected, precluding the use of this technique

in this interesting temperature range. A program has been initiated to study the formation of precipitate free zones at grain boundaries in precipitation hardened alloys. Electron microprobe analysis is being utilized to investigate composition variations at grain boundaries in two aluminum alloys as a function of minor alloy additions and heat treatment. The specific heat of a series of polymers are being studied in the glass transition region in order to determine the effect of thermal history and heating rate in order to increase the range of analysis and to check on the theoretical descriptions which have been made of glass transitions.

Other programs in this area have centered on vapor-solid phase reactions. High temperature equilibrium vaporization studies have been pursued in order to determine the stability of the condensed phase and the thermodynamic properties. During this period, studies have centered on the mode of vaporization of cadmium selenide. In a reverse sense to these equilibrium vapor-solid phase studies, investigation has continued in the non-equilibrium reversible oxidation of aluminum.

The effect of changes of the nature of the deformation process by the use of ternary alloy additions is being studied for alloys of Beta-brass.

REVERSIBLE OXIDATION OF ALUMINUM

Senior Investigator:

G. S. Ansell

Previous work in this laboratory had shown that Al-Al₂O₃ SAP alloys heated in the hot stage of an electron microscope formed a reversible type of aluminum oxide that had not been previously reported. In order to determine the nature of this rather unexpected event, a program to study the formation of reversible oxides of high purity aluminum in a more controlled atmosphere has been undertaken. In this study, oxidation is being studied both in situ, in the hot stage electron microscope in an atmosphere of 10^{-7} torr ambient at the specimen stage, and in an ultra high vacuum system with 10^{-9} torr capability. Studies are now in progress using both systems to study the oxide formation as a function of the nature of the amorphous aluminum oxide previously formed on the aluminum specimen surface, the purity of the gaseous environment and the thickness of the aluminum specimen.

MARTENSITE TRANSFORMATION

Senior Investigator:

G. S. Ansell

This program is part of a continuing study of the kinetics and resultant strength characteristics of the martensite transformation in the Fe-C system.

Several approaches are being used in this study. In the first, the effect of solute elements of varying diffusivity in austenite upon the nature of athermal stabilization during rapid quenching is being studied. We have established that such rapid quenching increases dramatically, as

much as 200°F, the M_s temperature of 52100 steel. We now wish to establish the role of the solute elements in steel upon this aspect of the transformation kinetics. This program has centered about determining the effect of quench rate upon the M_s temperature of the Fe-C-X alloys in which the nominal M_s temperatures of these alloys are identical and the effect of the X element on carbon diffusivity is quite variable. This program is now in progress. The results to date indicate that the quench rate effect of the M_s temperature is directly related to the rate of carbon diffusivity in the austenite as predicted by the strengthening model previously proposed.

The second approach has been to relate the entire transformation kinetics to the flow stress characteristics of the austenite. Here it appears that the M_s temperature depends upon the shear strength of the austenite, the M_s temperature decreasing with increased shear strength, while the extent of transformation as a function of under-cooling below the M_s temperature increases with increased work hardening rate of the austenite. These programs are currently in progress.

PRECIPITATION KINETICS

Senior Investigator:

G. S. Ansell

The studies of the formation of precipitate phases from solid solutions have continued.

During this program period, the study has centered upon the solubility of interstitial elements in transition metal alloys, particularly of the group VIa element series. A theoretical analysis of the solubility of the interstitial elements in these alloys was made. It

was found that the change of system free energy as the interstitials are formed from the atomic state during the dissolving process is dominated by the electronic interaction. This electronic interaction energy is characterized by the energy band structure, a rigid band model being used for the case of these bcc alloys. The minimum exhibited in the density-of-states curve, caused by the overlapping of subbands, gives rise to an unusual free energy change. Numerical calculations predict the interstitial solubilities in good agreement with experimental results.

STUDIES IN PRECIPITATION HARDENING SYSTEMS

Senior Investigator:

G. Judd

The current investigation centers upon the study of the formation of precipitate free zones (PFZ) at grain boundaries in precipitation hardened alloys. These PFZ have been observed to have a deleterious effect on the mechanical and corrosion properties of these alloys and consequently, an accurate evaluation of the mechanisms involved in their formation would be of substantial use in alloy design and development.

At present, two different aluminum based alloy systems (Al-Zn-Mg, Al-Ge) are being studied by electron probe microanalysis as a function of various heat treatments and minor alloy additions. The effect of these variables on the composition profile at the grain boundary is being determined, and these results will then be correlated with observed properties.

In addition to these grain boundary studies, the facility has also been used to supplement research efforts in several other research groups. Three additional personnel have been trained to use the microprobe. A

computer program to facilitate quantitative analysis has been adapted to the Rensselaer computer system and is now operational. The increased number of trained personnel and the increased capability in quantitative analysis will probably result in a greater and wider use of this facility.

DIFFERENTIAL THERMAL ANALYSIS OF THE GLASS TRANSITION REGION

Senior Investigator:

B. Wunderlich

The experimental work on Dynamic Differential Thermal Analysis of Glasses has been completed with the conclusion of the thesis work of Stephen Wolpert. Poly(methyl methacrylate), polystyrene, poly(vinyl chloride) and polymeric selenium have been analyzed. The final paper of this work is being prepared at present and will be submitted in the next six months. A summary of the results was contained in the previous semi-annual report.

Further work in this general area has been taken over by Mr. Alex Weitz. The work is at present being directed toward two experimental improvements. First, it is tried to achieve experimental techniques capable of measuring the glass transition at elevated pressures. In cooperation with the Aero Research Corporation a new thermocouple system capable of withstanding 5000 atm pressure has been developed. It is expected that delivery and tryout of these thermocouple systems can be accomplished within the next six months. The other direction of research is to achieve faster heating and cooling rates in the glass transition region. Rates of several hundred degrees C per min. are being sought. The achievement of such high heating and cooling rates are necessary to

widen the range of analysis and to check on the theoretical description of glass transitions derived previously.

THERMODYNAMIC STUDIES AT HIGH TEMPERATURES

Senior Investigator:

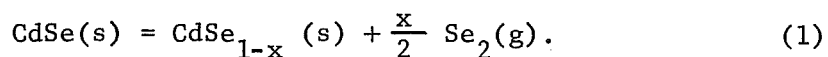
H. Wiedemeier

The objectives of this work are the determination of the thermodynamics of solid phase-gas phase interactions. Such investigations are of practical importance since a clear understanding of the solid-gas phase equilibria is essential for the preparation of materials employing vapor transport techniques.

It is surprising to find significant discrepancies in the literature concerning the mode of vaporization of cadmium selenide, which is usually considered to be a well-characterized material. The question of congruency is critical for the synthesis of CdSe, since deviations from stoichiometry have a decisive effect on the solid state properties of CdSe. In order to remove existing uncertainties Knudsen type vaporization studies were performed employing an automatic vacuum microbalance.

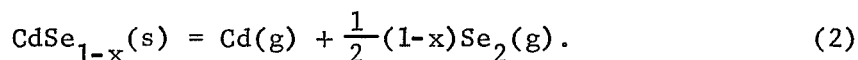
For this purpose high purity cadmium selenide was prepared from the resublimed elements. Chemical analysis and x-ray diffraction techniques verified that the compound was stoichiometric within narrow limits of experimental error and had the wurtzite structure. Before vaporization under equilibrium conditions the material was heated under vacuum to remove any condensed gases. During this procedure it was observed that CdSe lost a small amount of selenium at temperatures around 400°C according to the

reaction



Chemical and weight analysis and x-ray diffraction indicated that $x \ll 1$. The validity of reaction (1) was established through repeated experiments.

The material CdSe_{1-x} was then vaporized under Knudsen conditions at temperatures above 600°C . In a series of experiments various fractions of a given starting amount were vaporized. In each run the recovered sublimation products and the residue were characterized by x-ray diffraction and chemical techniques. The results of these experiments are concordant and demonstrate that CdSe_{1-x} vaporizes congruently according to the reaction



The determination of the degree of deviation from stoichiometry in CdSe_{1-x} is below the limits of x-ray diffraction techniques and of conventional chemical analysis. The experimental results are in agreement with other observations suggesting that the composition of CdSe synthesized by gas phase reactions is probably on the Cd-rich side of the homogeneity range of the stoichiometric composition. It will be the purpose of further investigations to determine vapor pressures according to the steady-state reaction (2).

NUCLEAR MAGNETIC RESONANCE

Senior Investigator:

P. A. Casabella

Nuclear magnetic resonance techniques, using the Na^{23} nucleus, have been used to study the temperature dependence of the spontaneous polarization of ferroelectric Rochelle salt in the vicinity of the phase transition at 24°C . These studies were undertaken because the magnetic

resonance method of determining polarization involves a static measurement, and thus might be more accurate than the usual AC bridge techniques near the transition. It was expected that the polarization should be proportional to the $(T_c - T)^{\frac{1}{2}}$ where T is temperature and T_c is the transition temperature. This prediction is based on a molecular field theory and has been borne out in other experiments, but deviations from this behavior should occur very close to the transition. The point at which the above behavior breaks down is an indication of the range of the interaction causing the ferroelectricity; the longer the range, the closer to the transition the molecular field theory holds.

The nuclear magnetic resonance experiments showed that polarization is proportional to $(T_c - T)^{\frac{1}{2}}$ to within 0.1°C of T_c . It was not possible to make measurements closer to T_c because the experiment involves measuring the separation between two resonances. For $T_c - T$ less than 0.1°C the resonances overlapped to such an extent that no further measurements were possible. An order of magnitude calculation indicates that deviations from the molecular field theory should occur when $T_c - T$ is in the range of 0.01°C to 0.1°C . Thus, the nuclear magnetic resonance method failed right on the fringe of the interesting temperature range.

PLASTIC DEFORMATION AND FRACTURE OF BETA BRASS ALLOYS

Senior Investigator:

N. S. Stoloff

The purpose of this investigation is to explore the possibility of improving the mechanical properties of a CsCl-type superlattice (β -brass) by changing the nature of the deformation process with ternary alloy additions.

Primary emphasis will be placed on the temperature and grain size dependence of the tensile properties and the associated deformation and fracture mechanisms. Alloying elements have been chosen on the basis of their expected effect on the ordering process and slip character of β -brass.

Sound, homogeneous, two-pound ingots were cast of the following compositions: Cu-46Zn, Cu-48Zn, Cu-45Zn-5Mn, Cu-45Zn-5Ni, Cu-45.5Zn-1Mn, Cu-45.5Zn-1Ni, Cu-48Zn-2Mn, Cu-48Zn-2Ni. Metallographic examination showed all to be single β -phase except Cu-45Zn-5Ni and Cu-45.5Zn-1Ni. Each ingot was forged between 500°C and 600°C and rolled 82-85 per cent at 200°C.

The recrystallization behavior for the above fabrication schedule of each alloy except Cu-45.5Zn-Ni has been determined. All of the single phase alloys can be recrystallized to uniform equiaxed grain sizes of 60-70 μ and 120-130 μ . These two grain size ranges will be used in the investigation. The Cu-45Zn-5Ni alloy can be recrystallized (130 μ grain size) and quenched as single β phase. Aging studies have been performed on this alloy. However, efforts to date to obtain a fine (<1 μ diameter) uniformly dispersed second phase have been unsuccessful.

Three fine-grained sheet-type tensile specimens 0.50" thick are presently being machined from each single phase alloy. These will be used to establish the specimen design and gripping arrangement necessary to determine the ductile to brittle transition temperature of each alloy.

A cylindrical (0.5 cm dia. x 5 cm long) single crystal with composition Cu-46Zn-3Mn was grown by the Bridgeman technique. The crystal orientation is close to $\langle 111 \rangle$ even though it was randomly nucleated. Sections were cut from both ends of the crystal and sent out for zinc and

manganese chemical analysis. No attempt was made to "level" (invert, remelt, and resolidify) this crystal. It is expected that the ternary manganese alloys will be the most difficult to obtain as single crystals due to the grain refining characteristics of the manganese.

First reports on three new studies; Ionic Defects and Electronic Properties of Transition Metal Oxides, Squeeze Flow of Non-Newtonian Fluids, and Solution Properties of Polymers; are presented here together with progress reports on the continuing studies of dispersion strengthened alloys; mechanical properties of crystalline and amorphous polymers, polymer rheology and composite material studies. Highlights of recent results include:

Creep data on sintered aluminum alloy powders which are significantly different from non-powder processed aluminum alloys. In sintered powder aluminum-magnesium alloys the creep rate is not apparently dependent on magnesium content.

Biaxial torsion pendulum studies on high impact polystyrene are yielding new insights on the toughness of this material which is related to localized yielding.

The formation of fibrous structure in cold-drawn crystalline polymers has been related to a localized yielding phenomenon not dissimilar to crazing in amorphous polymers.

Viscosity data on low molecular weight rubbers points to functional groups and intermolecular association as factors in determining viscosity-temperature dependence. Increased intermolecular association is reflected in increased temperature sensitivity of viscosity.

The causes of poor shear strengths in carbon fiber-epoxy composites has been identified as a weakness in fiber-matrix bonding which can be improved by alteration of the fiber surface. The key is to expose the edges of basal planes in the fibers' graphite crystal structure to form stronger fiber-matrix bonds.

SILVER-GALLIUM OXIDE ALLOYS

Senior Investigator:

F. V. Lenel

Preliminary steady state creep tests on silver-gallium oxide alloys produced by internal oxidation have been performed at temperatures between 600 and 800C and a series of stresses. The temperature dependence of the steady state creep rate appears to be the same as the self-diffusivity of silver which indicates that the rate controlling process in the creep of this alloy is the climb of dislocations through the silver matrix. A study of the stress dependence of the steady state creep rate at temperatures near 800C indicates that the creep rate is proportional to the first power of the stress at low stresses and proportional to the fourth power at higher stresses. This stress dependence is also in accord with a creep process controlled by climb of dislocation over second phase particles. It is intended to continue the creep tests and extend them to specimens prepared by decomposition of freeze-dried silver nitrate-gallium nitrate solutions to a silver-gallium oxide powder mixture and subsequent consolidation of the powder.

The study of the kinetics of internal oxidation in silver-gallium alloys is also continuing.

SINTERED ALUMINUM ALLOY POWDERS

Senior Investigator:

F. V. Lenel

Creep tests in a temperature range near 500C have been performed on specimens made from the atomized aluminum alloy powders obtained from

Illinois Institute of Technology Research Institute. The specimens had magnesium contents of 0.8, 1.05, 4 and 4.5 atomic percent. The stress dependence of the steady state creep rate of specimens produced from all four alloy powders was determined. The creep behavior is significantly different from that of specimens from aluminum-magnesium alloys not made from powder and, therefore, not containing a fine dispersion of aluminum oxide. In straight aluminum-magnesium alloy the stress dependence of the steady state creep rate changes with increasing magnesium content indicating the operation of a microcreep mechanism. No such change in stress dependence with alloy content was found in the dispersion strengthened alloys indicating that creep in these alloys is controlled by dislocation climb. Preliminary tests on the temperature dependence of the steady state creep rate of the alloys confirm this conclusion.

DISPERSION STRENGTHENING MECHANISMS

Senior Investigator:

G. S. Ansell

One aspect of the role of a second phase in dispersion-strengthening that has received little attention has been the necessity of strain compatibility at the two-phase interface in order to retain structural integrity. This effect has particular import as concerned not only with the initiation of voids and microcracks which can lead to fracture but also to the reduction in gross flow strength response. Previously, studies of the yielding behavior of two dispersion-strengthened alloys, TD nickel and an AL - Al_2O_3 SAP-Type alloy, demonstrated that the yielding behavior of two-phase alloys is sensitive to the level of normal

stress as well as the level shear stress. This is particularly important since up until this time, all theories of dispersion strengthening have been based only on shear stress dependent models. During the past program period, examination by transmission electron microscopy of the structure of deformed specimens of these alloys has begun to couple the mechanical behavior results with studies of localized plastic deformation and void formation during plastic strain. This work is currently in progress.

SUPERPLASTICITY

Senior Investigator:

L. A. Jackman

The mechanism responsible for the anomalous phenomenon of superplasticity exhibited by some metallic materials is being investigated by internal friction measurements. Since grain boundary sliding is one of the more strongly supported mechanisms proposed to explain superplasticity, an examination of the internal friction due to grain boundary sliding should be very informative. Al-Zn alloys with compositions in the range of the eutectoid have been selected for this investigation. Pure aluminum is also being examined for comparison purposes.

Internal friction attributed to grain boundary sliding is being observed with an inverted torsion pendulum apparatus constructed for this investigation. Activation energies associated with grain boundary sliding are being determined from these internal friction results and will be compared to activation energies obtained for the deformation of these alloys while exhibiting superplasticity. However, unlike the pure aluminum, the Al-Zn eutectoid alloy does not exhibit a well-defined peak, thereby making

activation energy determinations for the alloy quite difficult. However, a technique has been developed to determine these activation energies. The absence of a well-defined peak can possibly be attributed to the presence of three types of grain boundaries since there are two phases present. The influence of amplitude on the damping due to grain boundary sliding is also being determined, as are the effects of grain size, composition and heat treatment. Metallography is being performed on the specimens in order to characterize the grain size and the distribution of the phases.

BIAXIAL VISCOELASTIC STUDIES

Senior Investigator:

S. S. Sternstein

The biaxial torsion pendulum described previously has been used to obtain data on the effect of finite loading on the dispersion in high impact polystyrene (HIPS) and pure polystyrene (PS). There is relatively little effect of load on the dispersion in PS. However, in HIPS the dispersion shifts to higher frequency, the loss factor increases, and activation energy decreases as the axial load increases. These effects are reversible provided that the load is such that the local stress does not exceed the craze threshold stress described previously. When the craze threshold stress is exceeded, the shift to higher frequency, reduced activation energy, and increased loss factor are permanent. This suggests that the excess dispersion is associated with the locally yielded material, which is in the form of multitudinous crazes. The results are summarized in Figure 2, which shows the excess dispersion due to craze formation.

FIGURE 2

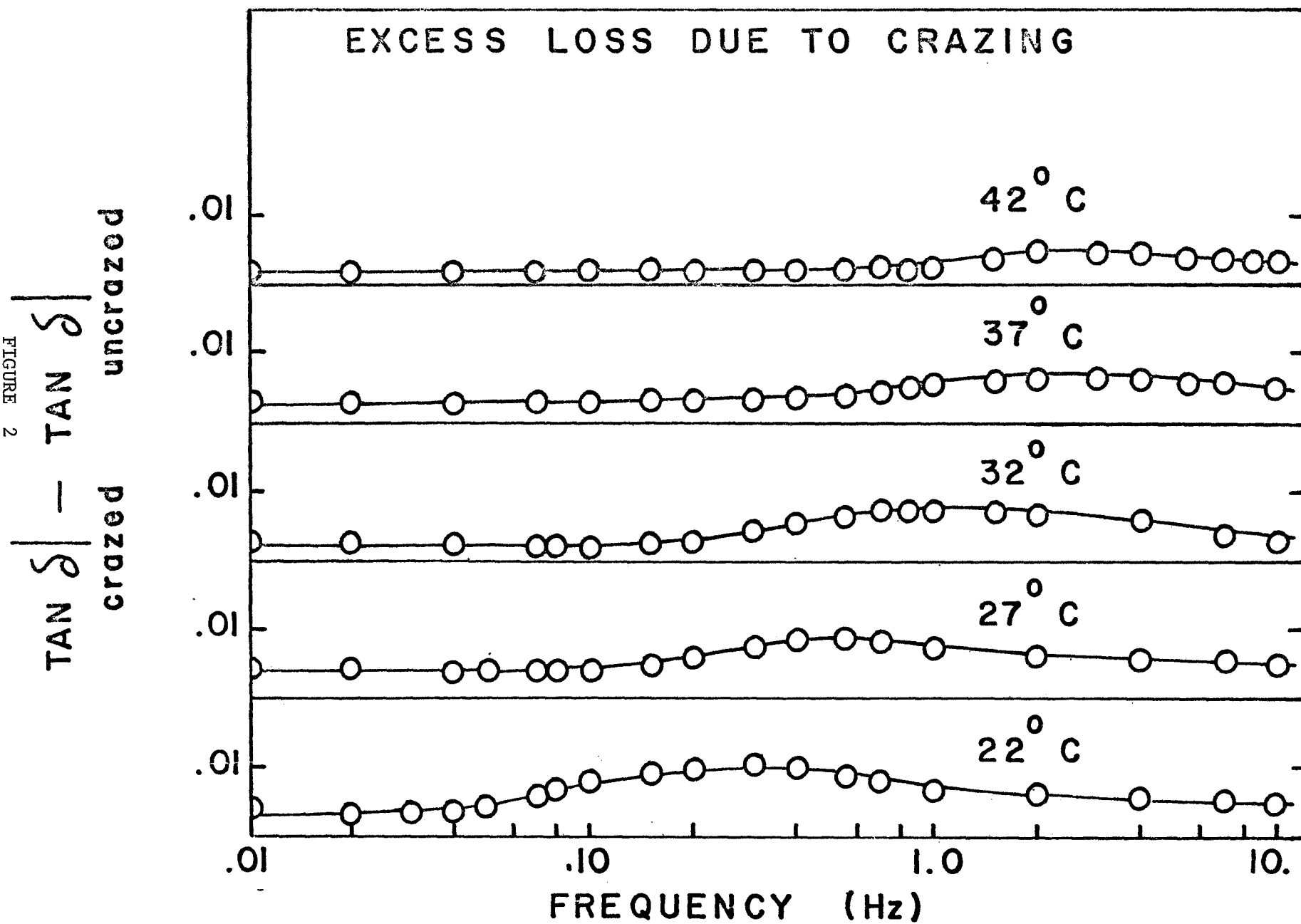


Figure 3 shows a comparison of the activation energies for crazed, uncrazed, and the excess dispersions. These results are being analyzed in terms of the micromechanics of the composite (HIPS) and the stress field criteria for yielding of glassy polymers reported previously.

Supported in part by N.I.D.R.

MORPHOLOGY AND PROPERTIES OF COLD DRAWN CRYSTALLINE POLYMERS

Senior Investigator:

David Hansen

One study of morphological changes on cold-drawing has been essentially completed. In general this work has provided some clarification of the interactions of small crystallites and larger units such as spherulites in cold drawing. In particular, the development of fibrous structure of fibrillation during cold drawing has been related to a process of forming localized dilations, similar to crazes. These dilations form during cold drawing and may orient and coalesce during the drawing to form a gross fibrillar structure. Within and around these dilations exaggerated local deformation yields a very fine scale fibrous structure.

Work is continuing on characterization of the long range elastic behavior of crystalline polymers. This study includes extensive experimental work on sample preparation (crystallization) to yield controlled variations in basic morphological parameters, long term creep and relaxation tests, and detailed morphological characterization of test specimens. It is not anticipated that conclusive results will be obtained in less than 12 months.

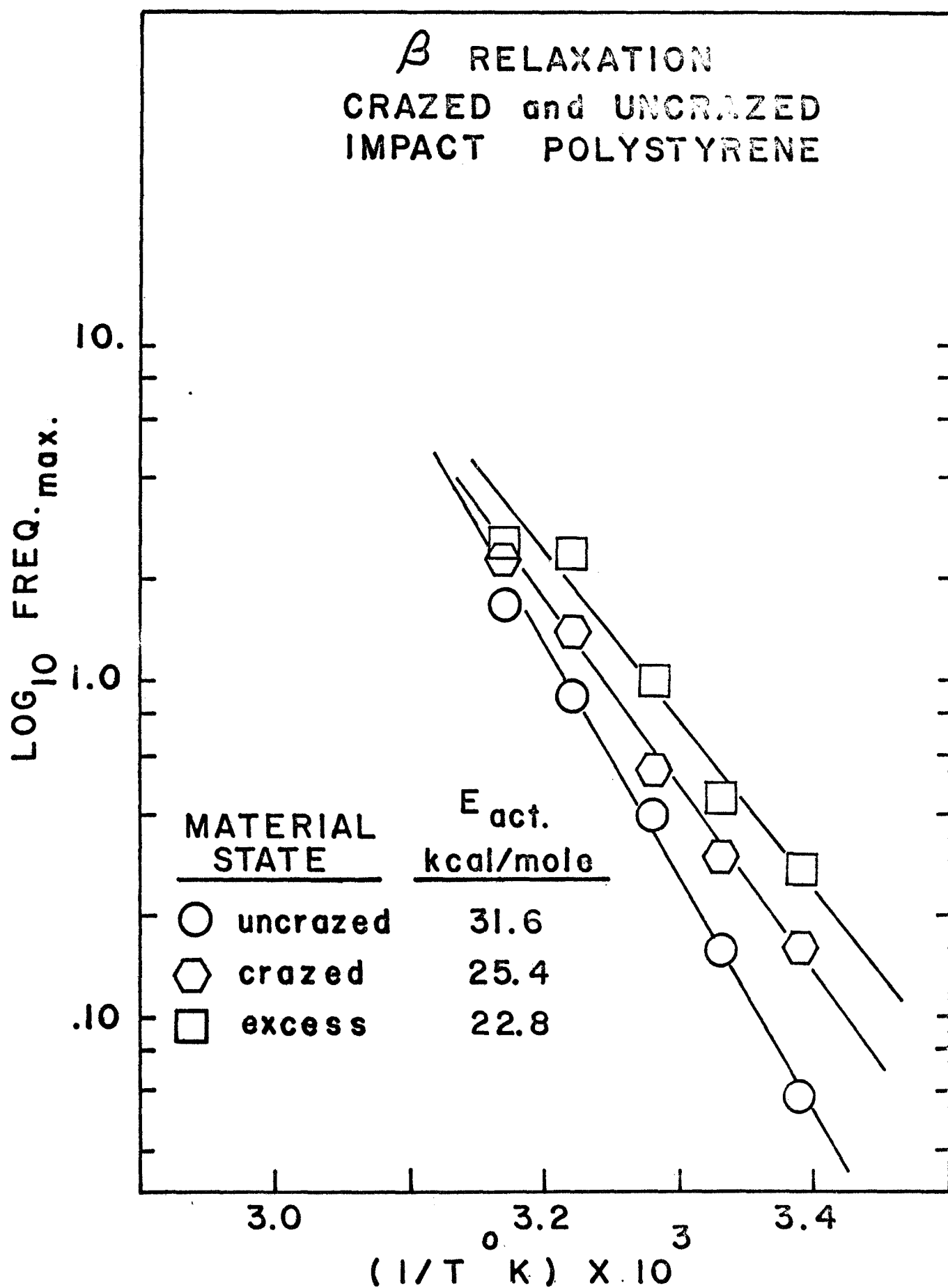


FIGURE 3

THE RELATION OF MOLECULAR STRUCTURE TO THE FLOW OF POLYMERS
AND POLYMER DISPERSIONS AS A FUNCTION OF TEMPERATURE AND SHEAR
RATE

Senior Investigator:

W. H. Bauer

The flow behavior of low molecular weight liquid rubbers was studied as a function of shear rate, temperature, functional groups and molecular structure. These polymers included carboxyl terminated polybutadienes, hydroxyl terminated polybutadiene, carboxyl and hydroxyl terminated butadiene acrylonitrile copolymers, mercaptan and xanthate terminated butadiene acrylonitrile copolymers and mercaptan and xanthate terminated polyacrylates. Measurements of the viscosity were made in the temperature range 15°C to 50°C at various shear rates. A cone and plate viscometer was used to cover the shear rate range 1 to 500 sec⁻¹.

All the materials studied displayed a region of shear thinning at higher shear rates. The samples also showed a limiting viscosity at low rates of shear. The viscosity data when plotted as log viscosity vs. log shear rate at constant temperature were found to be all superimposable onto one master curve by means of linear shifts. Activation energies for flow of the various samples calculated from the Andrade equation were found to be quite dependent not only upon the nature but also upon the quantity of the functional groups contained in the sample. Energies of Activation were found to have values characteristic of the molecular structure.

The log viscosity log shear rate flow curves for any particular sample at various temperatures were superimposable by means of linear

shifts in the x and y directions.

General conclusions were drawn from the data obtained. Association of polar functional groups contributed very heavily to the viscosity in the molecular weight range study. When functional groups contributing intermolecular association were present, a higher temperature coefficient of viscosity resulted, as shown by the increase of energy of activation with increasing amount of polar functional groups. Polymers with the highest amount of hydroxylcarboxyl and other groups capable of association showed the earliest onset of shear rate thinning as shear rate in flow was increased. Very large changes in viscosity at comparable molecular weights resulted from the introduction of polar groups into the molecular structure of the liquid rubber materials.

FLOW OF NON-NEWTONIAN FLUIDS

Senior Investigator: S. J. Kurtz

The first stage of the investigation of the flow of non-Newtonian fluids is nearing completion. This stage consisted of the design and construction of an instrument to measure the velocity and pressure distributions in the radial flow of non-Newtonian fluids.

SOLUTION PROPERTIES OF POLYMERS

PROPERTIES OF VINYL ACETATE: VINYL ALCOHOL COPOLYMERS

Senior Investigator: S. Krause

A study of the lowest molecular weight analogs of these polymers has begun. Before studying the solution properties of these copolymers,

we intend to investigate carefully the circumstances under which random and block copolymers are formed from vinyl acetate homopolymer and from vinyl alcohol homopolymer. Our first investigations are concerned with the two low-molecular weight compounds 1,3-butanediol and 2,4-pentanediol.

Both mono-acetates and the diacetate of 1,3-butanediol have been prepared and their purity is presently being investigated. If pure, these will be our first model compounds for high resolution nuclear magnetic resonance and for infrared studies.

Ion exchange columns are being set up for the separation of the optical isomers of 2,4-pentanediol using the properties of their borate complexes. The meso-isomer is the lowest molecular weight analog of isotactic poly(vinyl alcohol) while the d and l isomers are both analogs of syndiotactic poly(vinyl alcohol). The separated isomers will again be used to make the mono- and di-acetates for use as model compounds, and they will also be used to study the rates of esterification as a function of tacticity.

Work with the isomers of 2,4,6-heptanetriol is planned for the future.

GRAPHITE FIBER-EPOXY COMPOSITES

Senior Investigator:

R. J. Diefendorf

The cause of the poor shear strengths of carbon fiber-epoxy composites has been investigated. Working with x-ray and electron diffraction and polarized light microscopy, the structure of the graphite

crystallites within the carbon fibers was obtained. Polyacrylonitrile based fibers were shown to have structures similar to that of a rolled up newspaper. Rayon based fibers had random interior structures, but had a skin of basal planes covering the surface. Improved composite properties are based on the alteration of the fibers' surfaces, so that edges of the basal planes take part in the bonding between the crystallites in the fibers and between the fibers and matrix. A basic understanding of the shear strength of carbon fiber-epoxy composites has been obtained from the investigation of the fibers' structure.

IONIC DEFECTS AND ELECTRONIC PROPERTIES OF TRANSITION METAL OXIDES

Senior Investigator:

R. K. MacCrone

The electronic properties of the ionic defects in TiO_2 are being investigated in their own right, and also being used to investigate the ionic defects themselves.

A defect pair in iron doped TiO_2 is presently under investigation. At low magnetic fields the symmetry of the dielectric effect due to the predominant defect is that of the TiO_2 lattice, while at high fields the symmetry is that of the interstitial site. Various defect models are being considered whose validity will be tested with doped crystals.

Exploratory measurements on other transition metal oxides, (NiO and Fe_3O_4) are also being made.

In this section are reported experimental programs having as their primary aim to understand an electronic or physical property of a material per se rather than use the property as a tool toward understanding other aspects of the solid. As in other sections a large variety of materials are being studied by diverse techniques.

This has lead to interaction among investigators studying similar materials using different techniques. During the last six months the thermal conductivity of carefully characterized polyethylene samples has been measured as a function of crystallinity. It is felt that the change in thermal conductivity may be due to lamellar thickness. In addition to a continuation of the measurements at these temperatures, liquid helium temperature measurements of the thermal conductivity and heat capacity are being planned by a different group. The anelastic relaxation measurements in polymers reported on in this section in the last report have been moved to the Structural Characterization section because of their relation to low temperature specific heat measurements reported there by another group. This relation will be pursued in the future together with acoustic attenuation and spin-lattice relaxation time measurements.

Work begun under this contract continues to attract outside support.

IRREVERSIBLE THERMODYNAMICS OF THE SOLID STATE OF LINEAR HIGH
POLYMERS

Senior Investigator:

B. Wunderlich

During the last half year an extensive study of the chemical reaction of paraxylylene to poly-paraxylylene has been made. It was shown that there are two possible ways of addition of monomer to the growing polymer chain. For polymerization below the glass transition temperature it is expected that a rather poorly crystalline polymer is formed. Initial experiments at a higher condensation temperature have yielded polymer of greater perfection. The experimental set-up has been perfected and it is expected that within the next half year a larger series of polymerizations under varying conditions can be carried out.

Equipment and materials have been ordered for the analysis of the condensation of metaphosphates. Initially, the resulting metaphosphates will be analyzed by electron microscopy and x-ray diffraction to find a comparison with the organic linear high polymers. Parallel studies supported by the National Science Foundation on the polymerization of polyamides have been initiated and will be reported upon in this spot in the future because of their similarity. The latter work is being carried out by Charles Noll and Richard Bopp.

THERMAL CONDUCTIVITY OF CRYSTALLINE POLYMERS

Senior Investigator:

D. Hansen

Four samples of linear polyethylene (Marlex 6050) crystallized

to a specific gravity of 0.97 were annealed at different temperatures. Annealing at successively higher temperatures produced a corresponding increase in thermal conductivities measured between 20°C and 100°C.

<u>Annealing</u>	<u>Conductivity Calories/cm sec°C</u>
None	12.0×10^{-4}
100 hours at 126°C	15.2
120 hours at 127°C	15.2
290 hours at 128°C	16.3

The increase in thermal conductivity is probably associated with increases in thickness of the lamellar crystals of the polyethylene. Continuation of this work will focus on preparations of oriented crystalline specimens and detailed characterizations of structure by x-ray diffraction and electron microscopy together with thermal conductivity measurements.

SECOND ORDER ELASTIC CONSTANTS

Senior Investigator:

G. L. Salinger

The reanalysis of the measurements of the elastic constants of mercury was continued. The calculations are now complete.

The measurements of the velocities of longitudinal and transverse velocities of sound in polymers has been halted until a new cryostat can be put into operation since it will become much easier to make the measurements. This is a cryostat capable of maintaining temperature between 2 and 300°K.

The velocity of sound in some epoxy resins was measured to check an extrapolation to lower temperatures of heat capacity measurements made

between 1.7 and 4.2°K and reported in the literature. It was found again that such extrapolations in amorphous solids are very dangerous because of the large excess heat capacity due to localized non-acoustic modes.

A theory relating these non-acoustic modes and the attenuation of ultrasonic waves is being worked on in preparation for attenuation measurements which also will be carried out as soon as the cryostat is available.

Funds from a DOD Themis grant and National Science Foundation grant are also being expended in this effort.

THIRD ORDER ELASTIC CONSTANTS

Senior Investigator: H. B. Huntington

The measurement of third order elastic constants in NaCl by the beam mixing technique has been completed for two interactions in the (100) plane. In each case the longitudinal beam at the sum frequency has propagated down a crystalline direction of high symmetry while the two transverse beams were polarized perpendicular to the interaction plane and oriented in particular directions as determined by their frequency ratio. The measurements of conversion efficiency gave determinations of combinations of elastic constants. For longitudinal wave down the (100) axis,

$$\frac{c_{12} + c_{144}}{c_{11} + c_{166}} = -2.85 \pm 0.73$$

and for longitudinal waves down the (110) axis,

$$\frac{c_{11} + c_{12} - 2c_{44} + c_{144} + c_{166} - 2c_{456}}{c_{11} + c_{12} + 2c_{44} + c_{144} + c_{166} + 2c_{456}} = -0.580_3 \pm 0.0025.$$

These values turn out to be nearly half way between those measured by Chang in this laboratory and by Swartz at Illinois by different techniques.

SEMI-CONDUCTION IN GLASS

Senior Investigator:

R. K. MacCrone

Support for the experiments on $\text{Fe}_2\text{O}_3\text{-PbO-SiO}_2$ glass systems has been obtained from the National Science Foundation. We appreciate the National Aeronautics and Space Administration support which allowed us to initiate these experiments and bring them to a state where other support could be requested.

LOW TEMPERATURE MAGNETIC PROPERTIES OF DILUTE ALLOY SYSTEMS

Senior Investigator:

M. P. Maley

A Mössbauer effect spectrometer is being used to study the magnetic behavior of very dilute Fe impurities in non-magnetic metals. Measurements of the magnetic hyperfine field at the Fe^{57} nucleus yield information concerning the magnetic response of the electrons surrounding the impurity in the metal. A cryostat system capable of regulating source temperature between 1.2°K and 300°K is nearing completion, and a superconducting solenoid provides magnetic fields up to 62 kOe. Much current effort has been directed toward an understanding of the localized moment problem following the work of Kondo in 1964. Experimental and theoretical work indicating the formation of a correlated, many-body singlet state at low temperatures has stimulated much of the interest. Recent theoretical work has shown that the experimental results can also be described by a

model of spin-fluctuations in an otherwise non-magnetic system. Recent experimental work has indicated that the Zn(Fe) system may be one in which the spin-fluctuation times have become comparable with ordinary thermal fluctuation times. We are presently preparing Mössbauer sources of Zn(Fe) with the intention of looking for the effects of fluctuating hyperfine fields upon the Mössbauer spectra.

Studies of corrosion of composite alloys are continuing. Work has been done on a variety of alloy systems, including boron reinforced aluminum.

Another program is concerned with studies of bio-galvanic batteries for medical devices. In vitro laboratory experiments have been completed, while in-vivo experiments utilizing rabbits will soon begin.

A program on stress corrosion of magnesium base alloys described in the previous report has been terminated.

CORROSION OF COMPOSITES

Senior Investigator: N. D. Greene

Studies of the corrosion and the electrochemical characteristics of metallic composite structures continue. A report describing the corrosion behavior of fiber reinforced metals has been issued and submitted for publication. A second report covering the localized corrosion of duplex stainless steel is being prepared.

Currently, boron reinforced aluminum composites are being examined for evidence of galvanic corrosion susceptibility.

IN VIVO ELECTROCHEMICAL POWER SOURCES

Senior Investigator: N. D. Greene

This program is designed to determine the feasibility of powering cardiac pacemaker and other internal devices by bio-galvanic batteries. In vitro laboratory experiments to determine power outputs, electrode life, cell efficiencies and voltage output have been completed and a report is being prepared.

In vivo experiments utilizing bio-galvanically powered radio telemetry units will begin shortly. It is anticipated that small animals (e.g. rabbits) will be employed to detect possible tissue reaction effects.

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Billmeyer, Jr., Fred W., Livesey, P. J.

"Particle Size Determination By Low-Angle Light Scattering: New Instrumentation and a Rapid Method of Interpreting Data"

Published in Journal of Colloid and Interface Science, Vol. 30, No. 4, August 1969

Billmeyer, Jr., Fred W., Kelley, Richard N.

"Evaluating Dispersion in Gel Chromatography Dispersion Due to Permeation"

Submitted to Analytical Chemistry

Greene, N. D., Ahmed, N.

"Corrosion of Filament Reinforced Metal Matrix Composites"

Submitted to Journal of Composite Materials

Salinger, G. L., Choy, C. L., Chiang, Y. C.

"Thermal Conductivity of Amorphous Polymers Below 1°K"

Submitted to Physical Review Letters

Sternstein, S. S., Ongchin, L.

"Yield Criteria For Plastic Deformation of Glassy High Polymers in General Stress Fields"

Submitted to A. C. S. Polymer Pre-prints

Wiedemeier, Heribert, Sigai, A. Gray

"Phase Studies of the Systems Mn-S, Mn-Se, and MnS-Mn-Se"

Published in High Temperature Science, Vol. 1, No. 1, April 1969

Wunderlich, Bernhard

"Crystallization During Polymerization"

Submitted to IUPAC Symposium on Macromolecular Review, Budapest, Hungary

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