Experimental Phonon Physics

Progress Report

April 1, 1975 - March 31, 1976

R. O. Pohl and A. J. Sievers

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During this past year, our research efforts have included the following topics:

- (1) Thermal properties of glasses and disordered crystals
- (2) Effect of neutron irradiation on the thermal properties of vitreous SiO_2
- (3) Thermal properties of compacted and sintered microcrystalline solids
- (4) Search for the amorphous phase of solid oxygen
- (5) Lattice defect modes
- (6) Far infrared properties of glasses
- (7) Far infrared properties of semimetals
- (8) Far infrared properties of semiconductors
- (9) Far infrared absorption by small metal particles

In the following, we want to summarize the success achieved to date:

1. Thermal properties of glasses and disordered crystals

A careful study of the specific heat and the thermal conductivity of different samples of the same amorphous material, differing only by the previous thermal treatment and/or chemical purification has shown, much to our surprise, that the linear specific heat anomaly is indeed somewhat sample dependent. In As_2S_3 , B_2O_3 , and $\text{CaK}(\text{NO}_3)_3$ we have been able to vary the anomaly by a factor of two. This, in itself, would not be too surprising, since either accidental impurities, or some atomic rearrangement could, conceivably, exist in differing amounts in different samples. Amazingly, though, the thermal conductivity turned out to be sample independent. This finding demonstrates that the connection between the anomalous states as seen in specific heat measurements, and the phonon scattering as observed in thermal conductivity or ultrasonic attenuation, is in fact not as close as has been previously assumed. Furthermore, it is the phonon scattering that appears to be truly intrinsic, whereas the specific heat is not. In fact, the possibility of someday finding a glass whose low temperature specific heat follows the Debye prediction ($\propto T^3$), cannot be excluded with certainty at this time.

In an attempt to study the dipole moments of the phonon scattering states in glasses, we measured the thermal conductivity of a thin plate of silica in an electric field of 10^5 volt/cm. The objective of this experiment was to change the density of states of the phonon scatterers and thus change the thermal conductivity. Recent measurements of the dielectric function of silica by the Grenoble group (Hunklinger et al) had been interpreted with the assumption of a constant density of states and a dipole moment of 0.3 Debye. Our measurements showed no effect of the electric field on the thermal conductivity, to within our experimental accuracy. This experiment can be understood if we assume that the dipole moments of the scattering states

are as large as determined from the dielectric measurements. In that case, however, the density of the states must be constant to within 6% over the range of the phonon frequencies responsible for the thermal conductivity in the temperature range investigated. Alternatively, the phonon scattering states could have little or no relation to the states seen in dielectric measurements, and have indeed much smaller dipole moments. This question had to be left unanswered.

As reported in last years Progress Report, we had begun to search for glassy anomalies (i.e. specific heat and thermal conductivity) in highly disordered crystalline solids. The objective of this search was to determine at what degree of perturbation of the crystalline order a solid begins to show the glassy anomalies. The reason for this work is that one might have a better chance of understanding the anomalous states if they could be produced in a hopefully controlled manner in crystalline solids. We have looked at a number of disordered crystals:

High purity lead, plastically deformed to dislocation densities $\sim 10^{12} \text{ cm}^{-3}$ and kept at N_2 - temperatures during deformation in order to obtain maximum dislocation density. The sample was then mounted and cooled for the specific heat measurement without letting it warm up. The specific heat (in the superconducting state) was equal to that reported for single crystal lead.

KBr: KI, at certain mixing ratios, is known to crystallize in three different compositions. The crystallites, which are all oriented in the same way (i.e. the crystal still has the (100) cleavage planes characteristic for alkali halides), measure $\sim 10^3 \text{ \AA}$ in diameter. Neither thermal conductivity nor specific heat showed amorphous behavior.

Niobium - Zirconium alloys are known to exist in two rather similar phases, at least for certain mixing rations. Electron microscopic, neutron scattering, and Mössbauer effect investigations have given evidence that these

phases are not stable even at low temperatures, but tend to switch back and forth, at least at temperatures as low as 77°K. Liang-fu Lou, a post doctoral research associate supported by the Material Science Center, has found that this material does indeed show both an anomalous thermal conductivity and specific heat characteristic for glasses. He has explained his findings with the model of a tunneling motion of atoms which give rise to the crystalline phase fluctuations between the omega and the beta phase.

Slack et al at G. E. had studied the thermal conductivity of several boron compounds and had found it to be like that of impure crystalline solids. In YB_{66} , however, they observed a conductivity whose absolute magnitude and temperature dependence strongly resembled that of amorphous solids. From Dr. Slack we obtained several samples of YB_n , with n varying between 62 and 68, and found thermal conductivities very similar to that found by Slack et al. This is particularly interesting, since only the yttrium doping appears to be randomly distributed, while the boron atoms form a crystal lattice.

Finally, we have studied natural flint stone as a natural representative of a highly disordered crystalline solid. Both thermal conductivity and specific heat are similar to those of glasses. Transmission electron micrographs and electron diffraction pattern have recently given evidence, however, that flint is at least in part amorphous. Hence, before any conclusions can be drawn, we will have to explore the structure of this material more carefully.

2. Effect of neutron irradiation on the thermal properties of glasses

As mentioned in the last Progress Report, we have found that high energy neutron irradiation increases the thermal conductivity of silica at intermediate temperatures, while it leaves the conductivity in the $T < 1^\circ K$ region where the conductivity varies as $\sim T^2$, essentially unchanged. No more data has been obtained during this past year, since all our efforts to obtain samples were unsuccessful. Recently, however, Dr. White loaned to us a

heavily irradiated sample which is also large enough to allow specific heat measurements. Hence, this work will be resumed in the coming year.

3. Thermal properties of compacted and sintered microcrystalline solids

As another attempt to simulate amorphous solids, we have studied the specific heat and thermal conductivity of compressed crystalline powders and ceramics. As was to be expected, the conductivity in these materials is essentially determined by the contacts between the grains and is, therefore, not a characteristic quantity. The specific heat, on the other hand, had been found to be very similar to that of amorphous solids, as reported in last year's Progress Report. Since then, however, it has become clear that adsorbed gases or moisture play an important role in the low temperature specific heat in this class of materials. Although it is entirely unclear why a monomolecular layer of water on an Al_2O_3 grain a few thousand Angstrom in diameter should enhance the specific heat at 0.1K (how can these molecules have such low excitation energies?), nevertheless, our findings have made it clear that our present technique of studying small particles, without attempts at eliminating surface adsorption, lead to results which cannot be easily interpreted.

Consequently, we have concentrated on polycrystalline materials with no exposed surfaces, like glass ceramics. During the past year, we have mainly searched for suitable materials. Those have recently been located at Owens-Illinois, we have obtained samples, and we hope to carry out the thermal measurements shortly.

4. Search for the amorphous phase of oxygen

During the past year, we have embarked on a new venture, namely the search for amorphous oxygen. Its existence has been suspected as well as been denied in previous studies. From the available information, however, Stephen Gregory, who joined the group last May, concluded that it must exist if the melt is

cooled sufficiently rapidly. He designed and built a cryostat which allowed such a rapid cooling (from 77K to 4K in times much shorter than 1 minute), and using measurements of magnetic susceptibility, has recently found the first evidence for the amorphous phase.'

We believe that a detailed study of this material would be highly fruitful for a variety of reasons: Firstly, it is a chemically simple solid, which can be produced in high purity. Its glass transition temperature is in a range in which the low temperature physicist has much experience. Chemical contaminations typical for high temperature sample preparation is negligible. Secondly, amorphous oxygen should have very interesting magnetic properties. For these reasons, we consider the preparation of amorphous oxygen to be a major achievement.

5. Lattice defect modes

This last year Barker and Sievers finished up their survey of "Optical Studies of the Vibrational Properties of Disordered Solids" which was published in Rev. Mod. Phys. We quote from the abstract: "Since approximately 1950 an increasing portion of experimental solid state physics research has been concerned with studying defects in crystals. This trend might appear to be a rather belated recognition that most of the materials we come into contact with have a random structure. In fact the theoretical understanding and controlled preparation of compounds with defects or random structure has been very slow in developing. The present paper examines and reviews our knowledge of the lattice vibrations associated with defects. The coverage is extremely broad, as shown by the table of contents. It includes localized and resonant modes of isolated defects as well as the modes in highly disordered mixed crystals and glasses. It is primarily a review of experimental work but theoretical results are included where the latter explain or predict significant features. In order to be self-contained several sections of the

paper deal entirely with theoretical matters. There is a chapter on explicit solutions of the linear chain vibration problem and a short chapter on Green's function methods. The review emphasizes the infrared absorption and Raman scattering of defects. This is simply because other techniques have not yielded nearly so much information. Neutron scattering and electron tunneling are referred to only where they have shed light on certain systems. Extensive tables of defects and mode frequencies are included for each type of solid. The major solids which are reviewed include semiconductors, ionic compounds, organic compounds, and amorphous insulators."

6. Far infrared properties of glasses

The temperature dependence measurements of Mon and Sievers and Chabal and Sievers on the low frequency absorption coefficient of glasses has given new insight into the properties of the anomalous modes. This work has been described in APS meetings in Denver and New York and also has appeared as a Phys. Rev. Letter. We quote from one of the abstracts: "We have measured the absolute absorption coefficient for four different amorphous dielectrics, namely GeO_2 , SiO_2 and SiO_2 with 600 ppm H_2O between 1.2 and 4.2°K and PMMA between .54 and 10°K in the far infrared spectral region between 2 and 10 cm^{-1} . We are able to identify the energy level manifolds associated with some of the anomalous modes previously observed in the thermal properties of amorphous solids¹. Our measurements are consistent with the presence of two level systems over a limited range of temperature and frequencies. More extensive measurements to lower temperatures indicate widely spaced manifolds of energy levels. A temperature independent absorption coefficient has also been identified."

7. Far infrared properties of semimetals

The extreme sensitivity of the far infrared Faraday transmission technique on thick slabs of bismuth has resulted in the observation of a large number of sharp spectral features. Some of the absorption lines have been identified

with a weakly allowed harmonic series of cyclotron-like resonances associated with the holes. Other transitions with comparable strengths and similar field dependences have been identified during the past year with spin and combination resonances. This was the first identification of such far infrared resonances in a semimetal.

In addition we have also completed the first phase of our pressure dependent study of bismuth and these experiments have been described at the New York APS Meeting. We quote from the abstracts by E. A. Schiff and A. K. Chin: "Alfven-wave transmission studies in the far-infrared spectral region ($2\text{--}200\text{ cm}^{-1}$) are an effective and precise method for probing the electronic structure of bismuth. Extensive transmission studies in the Faraday geometry have now been conducted on bismuth under hydrostatic pressure; the experiments utilize a highly sensitive 0.3 K bolometer in conjunction with lamellar and Michelson Fourier transform spectrometers. Measurements of the Alfven-wave index of refraction for transmission along the bisectrix direction at 4.3 kbar were made as a function of magnetic field intensity and frequency; these results indicate a decrease in the carrier density of 4.7% per kilobar of applied pressure at 75 kG field intensity. In addition the positions of two low-field dielectric anomalies have been measured at 3 kbar along the bisectrix direction. Knowledge of these positions permits the determination of the static dielectric constant along the crystal's trigonal principal axis; the constant increases from its atmospheric pressure value of 60 by 2.3 units per kilobar." "Previous experiments have shown that the band parameters of bismuth are extremely sensitive to a hydrostatic pressure perturbation. We have used hydrostatic pressures up to 4.5 kbar to study the previously reported¹ triplet structure on the hole cyclotron resonance in bismuth oriented along the bisectrix direction. The fine structure is attributed

to inter-magnetic subband (IMS) excitons¹ whose binding energy is approximately the separation between the highest and lowest energy absorption line. The spacing has been observed to decrease from the atmospheric pressure value of 1.28 cm^{-1} to $1.1 \pm .1 \text{ cm}^{-1}$ at 3 kbar. The pressure dependence of a number of bismuth parameters was also measured in order to compare the observed decrease in the triplet splitting with the IMS model. Assuming a 1 bar value of 1.28 cm^{-1} for the binding energy of the IMS exciton, a binding energy of 1 cm^{-1} at 3 kbar is calculated in agreement with the measured $1.1 \pm .1 \text{ cm}^{-1}$ splitting."

8. Far infrared properties of semiconductors

Dr. K. Nagasaka has studied the photoconductivity and absorption spectra of n type CdS in the far infrared at large magnetic field strengths. He observed a new photoconduction process associated with a magneto-phonon resonance. The first order magneto-phonon resonance corresponds to a photon absorption process in which a single phonon is created by the strong electron-phonon coupling in CdS. In the next lowest order (2nd) absorption photon process two phonons participate. They may be both created or one may be created and the second destroyed. The electronic transitions between the neighboring Landau states participate in the magneto-phonon resonance but it is interesting that in this process the energy level of the final state of the electron is the same as the initial state.

9. Far infrared absorption by small metal particles

We have begun a systematic study of the far infrared absorption in small metallic particles. Our first set of measurements were published in the Physical Review and we quote from the abstract: "Far infrared transmission measurements were made on powder samples of Cu, Al, Sn, and Pb. The diameter of the particles ranged from 65 to 350 Å. All of the samples showed absorption which was very small at low frequencies and which increased more or less

linearly as the frequency increased. There was no change in the absorption as the temperature was varied from 1.2 to 20 K. For the smaller particles absorption curves calculated from the modified theory of Gor'kov and Eliashberg give a good description of the data, although clear choices between different energy-level ensembles cannot be made. Our measurements provide direct evidence that, for superconducting particles of diameter $\sim 100 \text{ \AA}$ and mean energy-level spacing $\sim kT_c$, the energy gap structure in the density of states is either much attenuated or is completely absent.

The following work is receiving MSC support.

Liang-fu Lou, a postdoctoral research associate with R. O. Pohl until September 1, 1975, has investigated the low temperature specific heat and thermal conductivity of the superconducting crystalline Zr:Nb alloy system. These properties show some striking resemblance to those of the dielectric glasses. There is some evidence that in this alloy system, atomic motion is possible at low temperatures. Lou has suggested that Zr:Nb may be a model substance which can be used to explain the thermal anomaly in dielectric glasses. Submitted for publication.

The following work is receiving NSF-RANN support.

Dr. R. Aurbach and Mr. D. Pramanik are investigating the optical properties of composite coatings made of small metal particles. Such a particulate metal coating on a low emissivity metal surface should provide the necessary temperature independent frequency selectivity for a solar collector.

The following work is receiving ARPA support.

Mr. A. Chraplyvy and Mr. G. Schmidt are studying the effectiveness of reactive atmosphere processing for removing the impurities from single potassium

bromide crystals. The thrust of this project is to obtain more transparent KBr window material for the 10 micron wavelength region of the electromagnetic spectrum.

As a summer project, Pohl has worked with the support of the Cornell Center for Science, Technology and Society, with a grant from the Sloan Foundation, on the problem of the health effect of natural and man-made carbon-14. Paper submitted to Nuclear Safety.

Invited Talks Given During 1975.

by R. O. Pohl: "Lattice Vibrations in Amorphous Dielectric Solids", University of Chicago; "The Anomalous Thermal Properties of Glasses at Low Temperatures", N.Y. Academy of Sciences Meeting on "The Glass Transition and the Nature of the Glassy State", "Phonon Scattering in Amorphous Solids", 2nd International Conference of Phonon Scattering in Solids, Nottingham, 1975; "Limits to Growth of Our Energy Consumption", University of North Carolina, Chapel Hill.

by A. J. Sievers: "Optical Studies of the Vibrational Properties of Disordered Systems" University of Delaware; "Particulate Coatings for the Direct Conversion of Solar Energy" Solar Thermal Conversion Workshop on Surface Coatings, ERDA; "A Solar Energy Transformer" Symposium on the Fundamental Optical Properties of Solids Relevant to Solar Energy Conversion" University of Arizona.

Papers Published During 1975

"The Thermal Properties of Sample Addenda Used in $T < 1\text{K}$ Specific Heat Measurements":

Specific Heat and Thermal Conductivity of GE 7031 Varnish, R.B. Stephens
Cryogenics July 1975, p. 420.

The Heat Capacity of Nichrome Resistance Wire, R.B. Stephens,
Cryogenics August 1975, p. 481.

"Short-Time-Scale Measurement of the Low-Temperature Specific Heat of Polymethyl Methacrylate and Fused Silica", W.M. Goubau and R.A. Tait, Phys. Rev. Lett. 34, 1220 (1975).

"The Intrinsic Low Temperature Thermal Properties of Glasses", R.B. Stephens, Phys. Rev. B, November 15, 1975.

"Phonon Scattering in Amorphous Solids", Proc. 2nd Conference on Phonon Scattering in Solids, Nottingham, 1975. L.T. Challis, ed., Plenum Press, 1975.

"The Far Infrared Properties of Polyamino Acids", W.J. Shotts and A.J. Sievers Biopolymers, 13, 2593 (1974).

"Plexiglass: A Convenient Transmission Filter for the FIR Spectral Region", K.K. Mon and A.J. Sievers, Appl. Opt. 14, 1054 (1975).

"Determination of the Hole Band Gap in Bismuth by Far-Infrared Magnets-Transmission", B.T. Smith and A.J. Sievers, Physics Letters 51A, 273 (1975).

"A Low Lying Defect Mode in $\text{CaF}_2:\text{Y}^{3+}$ ", J.A. Campbell, E.A. Schiff and A.J. Sievers, Physics Letters 51A, 470 (1975).

"Far Infrared Spin and Combination Resonances of the Holes in Bismuth", B.T. Smith, A.K. Chin and A.J. Sievers, Solid State Commun. 16, 1051 (1975).

"Far Infrared Absorption in Small Metallic Particles", D.B. Tanner, A.J. Sievers and R.A. Buhrman, Phys. Rev. B11, 1330 (1975).

"Temperature Dependence of the Far-Infrared Absorption Spectrum in Amorphous Dielectrics", K.K. Mon, Y.J. Chabal and A.J. Sievers, Phys. Rev. Lett. 35, 1352 (1975).

"Optical Studies of the Vibrational Properties of Disordered Solids", A.S. Barker Jr. and A.J. Sievers, Rev. Mod. Phys. 47, Suppl. 2, 1-179 (1975).

Theses Finished Furing 1975

"Low Temperature Thermal Properties of Granular Materials", R.H. Tait,
Ph.D. Thesis, June 1975.