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August 1973

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Lattice Vibrations in Non-Crystalline Solids*

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*Work supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-3151, Technical Report No. C00-3151-28 (unpublished).

Abstract

The specific heat of non-crystalline solids differs from that predicted by the Debye model by amounts much larger than is known for crystalline solids. This deviation is most pronounced at temperatures below 1°K. Near 0.1°K, the experimental specific heat approaches a linear temperature dependence and is up to 30 times larger than predicted by the Debye model. This paper describes Brillouin scattering experiments, and also measurements of the thermal conductivity in thin glass fibers. This work is aimed at elucidating the nature of the excitations responsible for this large specific heat. It is concluded that Debye phonons have sufficiently long lifetimes to be considered as good normal modes in non-crystalline solids and also that these phonons are the main carriers of heat at low temperatures.

1. Introduction

Specific heat measurements have contributed greatly to our understanding of excitations in solids. One of the best examples was the discovery that the specific heat of crystalline solids varies as T^3 at low temperatures. This led Debye to proposing that the thermal excitations of atoms in solids can be described by plane elastic waves, Debye phonons, as we want to call them for brevity in this paper. In Debye's model, which approximates the solid as a continuum, the specific heat $C_{v, \text{Debye}}$ is determined solely by the sound velocities, and at low temperatures approaches the T^3 law:

$$C_{v, \text{Debye}} = \frac{2\pi^2}{15} \frac{k_B^4 T^3}{h^3 \rho v_{\text{Deb}}^3} = 4.068 \times 10^{17} \frac{\text{erg}}{\text{sec}^3 \text{K}^4} \rho^{-1} \left(\left\langle \frac{1}{v_l^3} \right\rangle \right) \quad (1)$$

$$+ 2 \left\langle \frac{1}{v_t^3} \right\rangle T^3 = 234 \frac{Nk_B}{\rho \theta^3} T^3$$

where v_l , v_t are the longitudinal and transverse speeds of sound, v_{Deb} is the appropriate average of v_l and v_t , N the number density of atoms, ρ the mass density, k_B Boltzmann's constant, h Planck's constant $h/2\pi$, and θ the Debye temperature.

As examples, we show the specific heat of four chemically pure crystalline solids in Fig. 1, plotted as $C_{v, \text{exp}}/C_{v, \text{Debye}}$. The agreement between theory and experiment is generally very good, TiO_2 being the only substance which shows a marked

discrepancy, so far as we know. At low temperatures, the agreement becomes excellent. For $T < 10^{-2} \theta$, $C_{v,exp}$ and $C_{v,Debye}$ in practically all crystals agree to within the experimental errors. That much about crystalline solids.

In this lecture we want to review the work on a low temperature specific heat anomaly in non-crystalline solids and also to describe current work aimed at clarifying the role of Debye phonons in these solids.

2. Specific Heat of Non-crystalline Solids

The experimental facts for non-crystalline solids are easily summarized: They all have specific heats larger than predicted by the Debye model. Fig. 2 shows $C_{v,exp}$ of SiO_2 in its crystalline and in its amorphous phases (Zeller and Pohl 1971). The dashed line represents the Debye prediction for crystalline SiO_2 . Since the Debye temperatures of the two phases are quite similar ($\theta_{crystal} = 550^\circ K$; $\theta_{glass} = 500^\circ K$), the dashed line also represents the Debye prediction for the glass to a good approximation. In contrast to the good agreement between $C_{v,exp}$ and $C_{v,Debye}$ for the crystalline phase at all temperatures, and in particular below $10^{-2}\theta$, in the glassy phase $C_{v,exp}$ exceeds $C_{v,Debye}$ rather markedly. This discrepancy becomes particularly noticeable below $10^{-2}\theta$, in which temperature range $C_{v,exp}$ approaches a linear temperature dependence. The same behaviour has since been found in a total of 13 glasses,

without a single exception (Stephens 1973).

Recently, it has been claimed (Lasjaunias, et al. 1972, Lasjaunias 1973) that the low temperature specific heat in some cases (Se, B_2O_3) does not approach a strictly linear temperature dependence. Although we believe that unintentional paramagnetic impurities which are known to increase the specific heat of solids, were probably not adequately eliminated in some of these materials, we do not want to discuss these points in the present context, since they do not affect our main arguments. For more details, also see (Stephens 1973).

Some of the data are shown in Fig. 3, where the plot $(C_{v,exp}/T)$ vs. T^2 has been used in order to show that the polynomial expression

$$C_{v,exp} = c_1 T + c_3 T^3 \quad (2)$$

gives a good description of the data. In Fig. 4, we show, again as a typical example, the density of states of harmonic oscillators necessary to account for the measured specific heat in SiO_2 glass (Stephens 1973). Also indicated is the theoretical Debye density of states. Obviously, the specific heat measurements do not give any evidence of the existence of Debye phonons in non-crystalline solids.*

*A large density of states in glasses has also been inferred from nuclear quadrupole resonance work (Taylor and Rubinstein 1973).

One can think of two possible explanations: Either, Debye phonons exist in glasses as they do in crystals, but in addition, some unknown excitations exist which mask the specific heat of the Debye phonons. Alternatively, Debye phonons might not be good normal modes of the non-crystalline solid in the frequency range covered by the measurements, and the specific heat is determined entirely by the unknown excitations. Various observations led us to consider this second alternative seriously. Of them, we mention only one: Recent low temperature (0.1-1°K) ultrasonic measurements in the frequency range of 10^9 sec^{-1} have pointed to a remarkable fact (Hunklinger, et.al.1972, Golding, et.al. 1973): The ultrasonic attenuation was found to increase strongly with decreasing pulse power, see Fig. 5, demonstrating strong non-linear forces in the glassy solid. Although it was not possible to extrapolate these data to acoustic intensities characteristic for thermal phonon intensities, these data nevertheless gave rise to the suspicion that thermal Debye phonons might be too short lived to be considered as normal modes in the glass.

In the next two sections, we turn to two experiments which were undertaken at Cornell with the goal of deciding whether Debye phonons do exist and also, whether they are the dominant carriers of heat in non-crystalline solids at low temperatures.

3. Brillouin Scattering in Glasses

In the first investigation (Love 1973), Brillouin scattering was used to search for thermally excited Debye phonons with frequencies of $\simeq 2 \times 10^{10} \text{ sec}^{-1}$. Figs. 6 and 7 show the Brillouin spectra in vitreous SiO_2 and in a borosilicate glass at two temperatures. At 300°K and 36°K respectively, the strong Anti-Stokes and Stokes lines associated with the n -th and $(n + 1)$ th order respectively clearly indicate the existence of thermal transverse (T) and longitudinal (L) phonons in both glasses. Their velocities agree very well with those determined from elastic measurements. With decreasing temperature, the intensities of the Brillouin lines decrease linearly with temperature as expected for harmonic oscillators in the classical regime, see Fig. 8. The presence of longitudinal phonons is clearly observable at the lowest temperatures in both glasses, see Figs. 6 and 7. In the borosilicate glass, the observed Brillouin intensity at $T = 1.6^\circ\text{K}$ exceeds the theoretically expected intensity. This probably indicates sample heating by the laser beam (the sample fluoresced strongly). The Brillouin lines caused by transverse phonons were not detected below 20°K in SiO_2 (the equipment did not allow taking data between 2 and 20°K). In the borosilicate glass, a hint of transverse phonon peaks was seen at the lowest temperature, see Fig. 7, but the signal-to-noise ratio makes the identification somewhat un-

certain. From the widths of the Brillouin lines, the lifetimes of the longitudinal and the transverse phonons were estimated to be longer than 10 periods of oscillation at all temperatures. These results indicate that Debye phonons do indeed exist. Consequently, the separation of the density of states into Debye phonon states and into some other states, as done in Fig. 4, is justified, at least in the frequency range near $2 \times 10^{10} \text{ sec}^{-1}$ (quantum energies near $1.3 \times 10^{-16} \text{ erg}$).

4. Casimir Boundary Effect in Glasses

In Section 3, we learned that Debye phonons exist in glasses at low temperatures. Now, we want to explore their contribution to the heat transport. In other words, we want to learn whether the additional excitations observed in specific heat measurements can also carry heat. We will do this by studying the influence of the sample diameter on the thermal conductivity of glasses.*

* The detailed study of this subject is part of the Ph.D. Thesis research by one of the authors (R.B.S.).

In contrast to crystalline solids, whose conductivities depend strongly on their chemical composition and on their chemical and physical perfection, all non-crystalline solids have thermal conductivities which are practically identical,

see Fig. 9. Note in particular the conductivities below 1°K which are given by a power law

$$\kappa(T) \propto T^{\delta}, \quad (3)$$

where the range of δ lies between 1.8 and 2.0 for all glasses studied. It is in the same temperature range that the large linear specific heat becomes noticeable, and this led us to ask whether at least part of the heat is carried by these unknown excitations. The way we go about answering this question is as follows:

Let us assume that the heat is carried entirely by the Debye phonons. In that case, an average phonon mean free path $\bar{l}(T)$ can be determined from the experimental thermal conductivity $\kappa(T)$ through the relation

$$\kappa = \frac{1}{3} C_v v \bar{l}. \quad (4)$$

In Eq. (4) C_v is the specific heat of the heat carrying excitations only, and v is their group velocity. Hence, according to our assumption:

$$\kappa = \frac{1}{3} C_{v, \text{Debye}} v_{\text{Debye}} \bar{l}. \quad (5)$$

$\bar{l}(T)$ as derived from Eq.(5) is shown in Fig. 10 for three glasses. Our question is whether this mean free path is physically significant. We will try to answer this by introducing defects into the glass whose scattering cross section for phonons is known. Such defects could be isotopes (isotope

effect). One can convince oneself easily however, that their expected influence on the phonon mean free path would be as small as to be unnoticeable even under the most favorable conditions. The only other well understood phonon scatterer is the surface of the sample itself (Casimir boundary effect). A look at Fig. 10 shows that the phonon mean free path $\bar{l}$ for vitreous SiO_2 is 2×10^{-2} cm at 0.1°K . Hence, the thermal conductivity of a silica rod should become size dependent for rod diameters of that magnitude, provided our assumption is correct and $\bar{l}(T)$ is as shown in Fig. 10. Quantitatively, the total phonon mean free path $\bar{l}_{\text{tot}}(T)$ is given by

$$\frac{1}{\bar{l}_{\text{tot}}(T)} = \frac{1}{\bar{l}(T)} + \frac{1}{l_{\text{bd}}} \quad , \quad (6)$$

where, after Casimir:

$$l_{\text{bd}} \simeq d, \quad (7)$$

and d is the diameter of the fiber.

So far, data have been obtained on silica based glass fibers of $\simeq 60\mu$ diameter. These results are shown in Fig. 11. The upper curve was measured on a bundle of smooth glass fibers, as obtained from the manufacturer. Their conductivity was found to be identical in magnitude and temperature dependence to that of the soda-silica glass ($3\text{SiO}_2:\text{Na}_2\text{O}$) shown in Fig. 9. After chemically etching the fibers, however, their conductivity

was found to be noticeably smaller, see the lower curve in Fig. 11. The solid line drawn through the lower curve was computed from eqs. (5)-(7), using $\bar{\ell}(T)$ determined from the bulk glass, and $d = 6 \times 10^{-3}$ cm. The excellent agreement between experiment and theoretical prediction leads us to the conclusion that the assumption, namely that the heat in the glass is carried predominantly by Debye phonons, is indeed correct. This conclusion is justified in the temperature range in which the boundary effect has been observed, i.e. for $T < 1^\circ\text{K}$.

The reason why the boundary effect is absent in the smooth fibers is most likely specular reflection of the phonons by the smooth surfaces. This effect is known from crystals; Casimir's theory specifically requires a diffuse scattering at the surface, and this condition is met only if the surface is rough on the scale of or larger than the phonon wavelength. It is met on the etched fibers, but not on the smooth ones, as was shown by scanning electron microscopy.

This investigation, although still preliminary, lends confidence to the analysis of the conductivity in terms of Debye phonon mean free paths as shown in Fig. 10. Consequently, we believe that we can indeed determine Debye phonon lifetimes from thermal conductivity experiments in glasses. At a given temperature, the bulk of the heat is carried by a certain spectral range of Debye phonons, called the dominant phonons

(dominant phonon approximation (Zeller and Pohl 1971). For silica, the wavelength $\lambda_{\text{dom.}}$ of the dominant phonons is shown in Fig. 10. From this figure, it can be seen that below $T = 1^\circ\text{K}$, $\bar{\tau}(T)$ is of the order of $10^2 \lambda_{\text{dom.}}$, or that the dominant phonon lifetimes are 10^2 periods of oscillation. Because of the higher density of states of the transverse phonons the bulk of the heat is carried by those, rather than the longitudinal phonons. Therefore, these lifetimes are probably representative values for transverse phonons. In this sense, these measurements supplement the Brillouin scattering experiments described in Section 3, in which the most convincing evidence was obtained for long-lived longitudinal phonons.

5. Conclusion

The experiments described in this paper have provided us with the following picture: The specific heat of non-crystalline solids exceeds that predicted by the Debye model by a large amount, in particular below 1°K . Debye phonons do, however, exist at these low temperatures, and they also are the main carriers of heat. Their specific heat is simply masked by that of some other excitations of presently still unknown origin.

To-date, most of the theories proposed have concentrated on the frequency-independent, constant density of states of excitation responsible for the linear term in Eq.(2) which dominates the specific heat at the lowest temperature. However,

as a look at Fig. 4 shows, the physical reason for this separation of the excess density of states (the area between the two parabolae) is not clear. Conceivably, the large quadratic density of states responsible for the specific heat proportional to T^3 above 1°K could be simply caused by a different dispersion of the phonons in glassy solids, i.e. a bending away of the ω vs. k curve at phonon wavevectors smaller than customary in crystals. The constant density of states which dominates at low frequencies, however, certainly cannot be explained in such a way. The theoretical models used to explain these low energy states have invoked low lying electronic states which could possibly be connected with the bound states in the gap of amorphous semiconductors (Kaplan, et al. 1971, Redfield 1971). Also postulated have been atoms trapped in pores with a certain spread of diameter (Rosenstock 1972), and peculiarities of the phonon dispersion curves causing states of small energies with large wavevectors (Fulde and Wagner 1971, Takeno and Goda 1972). Neutron scattering is currently used in order to search for these states (Kim Carneiro and J. W. Wilkins, private communication).

The most detailed calculations have been made for a model in which certain atoms in the glassy structure are assumed to tunnel between almost equivalent equilibrium positions (Phillips 1972, Anderson, et al. 1972). Experimental studies undertaken

to test this model will be reported at this conference, and the reader is referred to these papers (Hunklinger, et al. 1973, Golding, et al. 1973).

In spite of many attractive aspects inherent in all of these different models, it appears too early to decide which if any of them to prefer. As we see it, the most serious problem they all face is the one that they must be general enough to be applicable to the wide variety of materials in which the anomalous thermal behaviour has been found. On the experimental side, far greater efforts are needed in order to search for ways of influencing the anomalous properties of glasses, or to simulate them in disordered crystals.

Thus it appears that both from a theoretical and an experimental viewpoint these phenomena continue to contain numerous challenges.

FIGURE CAPTIONS

Figure 1: Comparison of experimental specific heat $C_{v,exp}$ with the Debye prediction, plotted as $C_{v,exp}/C_{v,Debye}$. (KCl: Keesom and Pearlman 1953(b), Berg and Morrison 1957. Se: Anderson 1937, de Sorbo 1953, Fukuroi and Muto 1956, Lasjaunias 1969, 1973, Lasjaunias, et al. 1972. Ge: Keesom and Pearlman 1953(a), Hill and Parkinson 1952. TiO_2 : Sandin and Keesom 1969, Dugdale, et al. 1954, Morrison and Patterson 1954.)

Figure 2: Specific heats of SiO_2 in the glassy and in the crystalline phase, after (Zeller and Pohl 1971). References to earlier measurements can also be found in this paper. The theoretical Debye specific heat for crystalline SiO_2 is shown as the dotted line.

Figure 3: Specific heat of nine glasses. Data on polystyrene (PS) and polymethyl methacrylate (PMMA) (Stephens, et al. 1972). Data on Lexan after Cieloszyk and Salinger, private communication. In addition to the glasses shown in this figure, a linear anomaly has been found in glycerole, borosilicate glass (as used for Pyrex ware), GE 7031 dried varnish, and GeO_2 (Stephens 1973).

Figure 4: Densities of states $\left(\frac{\partial n(\hbar\omega)}{\partial(\hbar\omega)}\right)_{Deb}$ and $\left(\frac{\partial n(\hbar\omega)}{\partial(\hbar\omega)}\right)_{exp}$ vs. $\hbar\omega$ for SiO_2 glass,

assuming that the excess states are harmonic oscillators (Stephens 1973). Harmonic oscillators are frozen out roughly at $\hbar\omega/k_B T = 1/3$, so, for instance, all the states up to $\hbar\omega/k_B = 1^\circ\text{K}$ are involved in the specific heat at $1/3^\circ\text{K}$. The top scale on this figure shows the temperature at which an oscillator of energy $\hbar\omega$ gets thermally excited.

Figure 5: Ultrasonic attenuation in vitreous silica (Hunklinger, et al. 1972). See also the more recent work (Hunklinger, et al. 1973).

Figure 6: Brillouin spectra of fused silica at (a) 230°K , (b) 1.7°K . Rayleigh (R), longitudinal (L), and transverse (T) peaks are shown for the Anti-Stokes (A-S) and Stokes (S) shifts. Gain changes, as noted relative to the Rayleigh peak, were made as necessary (at dashed lines). The longitudinal Stokes peak is cut by the I_2 filter. The Rayleigh peaks in each scan belong to adjacent orders (Love 1973).

Figure 7: Brillouin spectra of borosilicate glass. The gains for both traces were adjusted such that the anti-Stokes longitudinal peaks coincided. In the low temperature, noisy trace, the transverse thermal phonon peaks are only barely detectable.

Figure 8: Brillouin peak intensities for borosilicate glass (open circles) and for fused silica (closed circles) as a function

of temperature. The theoretically expected temperature dependence of the intensities is indicated by the solid curves. The Anti-Stokes (A-S) intensity is proportional to the phonon occupation number, $\langle n \rangle$, where $\langle n \rangle = \left[\exp\left(\frac{h|\Delta\nu|}{k_B T}\right) - 1 \right]^{-1}$, while the Stokes (S) intensity is proportional to $\langle n \rangle + 1$. For $T \gg \frac{h|\Delta\nu|}{k_B}$ (i.e., $T \gg 1^\circ\text{K}$), both A-S and S intensities vary linearly with temperature. For $T \lesssim \frac{h|\Delta\nu|}{k_B}$, the A-S intensity should approach zero exponentially while the S intensity should become temperature independent. L and T represent longitudinal and transverse peaks respectively (Love 1973).

Figure 9: Thermal conductivity of non-crystalline solids. The scatter in the data is comparable to the line width, so smooth lines are shown for all samples. The data on As_2S_3 above 1°K are after A. J. Leadbetter, private communications; those on Lexan are after G. L. Cieloszyk and G. S. Salinger, private communication.

Figure 10: Average phonon mean free path $\bar{\ell}(T)$ after eq. 5 for crystalline SiO_2 and for vitreous SiO_2 , GeO_2 , and Se. At the top of the figure are indicated the phonon wavelengths and frequencies for SiO_2 (both vitreous and crystalline) in the dominant phonon approximation. The dashed lines represent model calculations (Zeller and Pohl 1971).

Figure 11: Casimir boundary effect in thin glass fibers. The open circles were obtained on smooth fibers. The solid line through them is the bulk conductivity measured on soda-silica glass, Figure 9. The closed circles were obtained on etched fibers. The solid curve through them was computed after eqs. 5-7, which are based on the assumption that Debye phonons are the sole carriers of heat.

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