isfied even for ions with velocities nearer to v_{Ti} so that bulk ion heating can result.

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Anomalous Thermal Properties of Glasses

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Experiments have shown that glasses, at low temperatures, possess an anomalous specific heat above that due to the lattice vibrations. Using two parameters I fit the contribution of a new excitation to the experimental specific-heat data. An experiment to test the theory is suggested.

The low-temperature specific heat of glass has been reported[1] to have an anomaly in that it is "excessive." This excess is above the T^3 dependence from lattice waves that one normally finds in crystals. Several explanations have been offered for this "excess" specific heat. In one assignment the "excess" specific heat has been attributed to localized low-frequency oscillations of molecules at voids[2] or to a localized two-level system.[3] Another explanation is that the excessive specific heat arises from the excitation of defects of the dislocation type.[4] In another explanation Fulde and Wagner[5] have constructed a propagator for low-lying phonons that is the basis of a semiphenomenological model into which they insert decay properties of these phonons. Takeno and Goda[6] show a contribution from the extra density of states from rotonlike excitations. To my knowledge there has been no experiment that unequivocally eliminates these explanations. I offer here an explanation similar to that of Takeno and Goda, which gives rather good agreement with some of the experimental results and is consistent with a general hypothesis concerning liquids and glasses that I have formulated[7] and with which I have had some good success in assessing numerous properties of liquids.

Stephens[1] has suggested that perhaps the phonon picture is not useful to describe the specific heat and heat conductivity of glasses and has suggested that another representation is needed. Zeller and Pohl[1] likewise have suggested that the anomaly in glass is specific to the amorphous state. My treatment is consistent with both of these points of view. In my treatment I propose that all liquids and glasses possess a new fundamental excitation.

This excitation is a localized region of somewhat lower density than the host matrix. Corre-

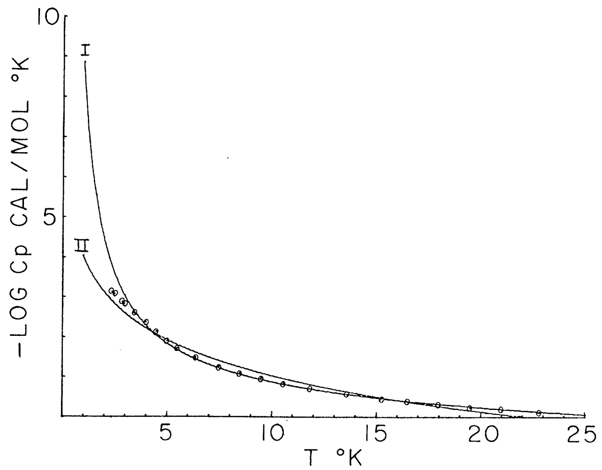

FIG. 1. Experimental values (Ref. 7) (circles) for $\ln C_p$ as a function of temperature. Curve I is from Eq. (2), and curve II is from kT^3 fitted at $T = 15.147$°K. Note the departure of the experimental points from the theoretical curve I beginning between 3 and 4°K.

spondingly a localized region of somewhat higher density may exist. The volume occupied by this localized region is of the order of a coordination volume. These localized regions have the property that they are free to propagate throughout the crystal.[8] It may well be that "soliton" solutions exist[9] for them, that is, a solution of a nonlinear differential equation, but I have not pursued this. In any case the statistical mechanics is similar to that given by Landau for rotons in liquid helium.

To illustrate the use of the excitations in explaining the "excess" specific heat in glass I choose the experiment of Antoniou and Morrison[10] on pure vitreous germania since their data are tabulated. In Fig. 1 I reproduce the data given by them (circles). I assume that the only contributions to the specfific heat come from the excitations. For the time being I will assume that the only role the phonons play is to absorb the annihilation energy of the excitations.

The energy of the existence in one molar volume, V, of the glass is

$$U=\frac{V}{2\pi}\exp(-\beta\epsilon_V)\int_0^\infty \frac{dk\, k^2[\epsilon_V+\hbar^2k^2/2m^*]}{\exp(\beta\hbar^2k^2/2m^*)-\exp(-\beta\epsilon_V)}, \tag{1}$$

where I have assumed the excitations obey Bose statistics. ϵ_V is the excitation formation energy, m^* is the effective mass, and $\beta=(kT)^{-1}$. The specific heat to order $\exp(-2\beta\epsilon_V)$ is

$$C_P=V\left(\frac{km^*}{2\pi\hbar^2}\right)^{3/2}\exp(-T_V/T)\epsilon_V T^{1/2}\left\{3+\frac{T_V}{T}+\frac{15}{4}\,\frac{T}{T_V}+\frac{\exp(-T_V/T)}{2^{3/2}}\left(\frac{15}{4}+2\frac{T_V}{T}+\frac{15}{8}\,\frac{T}{T_V}\right)\right\}, \tag{2}$$

where $\epsilon_V=kT_V$. In Fig. 1 I have plotted this function along with the experimental points and a T^3 dependence that fits one point. Values of T_V and $V(km^*/2\pi\hbar^2)^{3/2}\epsilon_V=K$ used are $T_V=20.5$°K (fitted value) and $K=0.047$ cal/mol°K (fitted value).

We observe from Fig. 1 that the function follows the experimental points from 3°K up to 25°K, and indeed as far as 50°K using data given by Zeller and Pohl.[1] The T^3 dependence in the same region departs significantly from the experimental points. However, below 3°K we see that the function [Eq. (2)] does not remove the anomaly, nor does the T^3 dependence, a fact that is well known.[1]

I proceed now to discuss the region $T<1$°K. It is apparent that Eq. (2) does not describe that region at all and in no way approaches the experimental values. Yet one feels that, since this representation was successful at higher temperatures, it should play a role at the lower temperatures as well. If the excitations are annihilated by a second-order (Raman) interaction with the phonons present, as one might expect, then as the temperature is lowered this process slows down considerably (as T^7).[11] Bringing the temperature down may "lock in" a nonthermal equilibrium excess number of excitations that would contribute a temperature-independent value to C_P at low temperatures. I will pursue this hypothesis.

Under the assumption that the number of excitations, N_L, that are locked in corresponds to the thermal equilibrium number at T_L (T_L between 1 and 5°K) we have

$$N_L=\left(\frac{m^*kT_L}{2\pi\hbar^2}\right)^{3/2}V\exp(-T_V/T_L), \tag{3}$$

where V is the molar volume of the glass. Further, if we assume that N_T shallow traps (one bound state, for simplicity) with binding energy $k\delta$ exist for these almost-free locked-in excitations, the number of excitations that are not in the traps and therefore free to conduct is[12]

$$N_F=\frac{N_LT^{3/2}}{Ge^{\delta/T}+T^{3/2}}, \tag{4}$$

where $G=N_T/(m^*k/2\pi\hbar^2)^{3/2}V$. The energy, U, of these free excitations is

$$U=N_Fk(\tfrac{3}{2}T+\delta). \tag{5}$$

The thermal conductivity is

$$K=\tfrac{1}{3}l(1.128)\left(\frac{2kT}{m^*}\right)^{1/2}\frac{1}{V}\frac{\partial U}{\partial T}, \tag{6}$$

where l is the collision distance of the excitations. Evaluating (6) we get

$$K=\frac{1.128}{3}\,l\left(\frac{2k}{m^*}\right)^{1/2}\frac{1}{V}kN_L\left\{\frac{T^2}{Ge^{\delta/T}+T^{3/2}}\left[\frac{15}{4}+\frac{3}{2}\,\frac{\delta}{T}+\left(\frac{3}{2}+\frac{\delta}{T}\right)\left(\frac{G(\delta/T)e^{\delta/T}-\frac{3}{2}T^{3/2}}{Ge^{\delta/T}+T^{3/2}}\right)\right]\right\}. \tag{7}$$

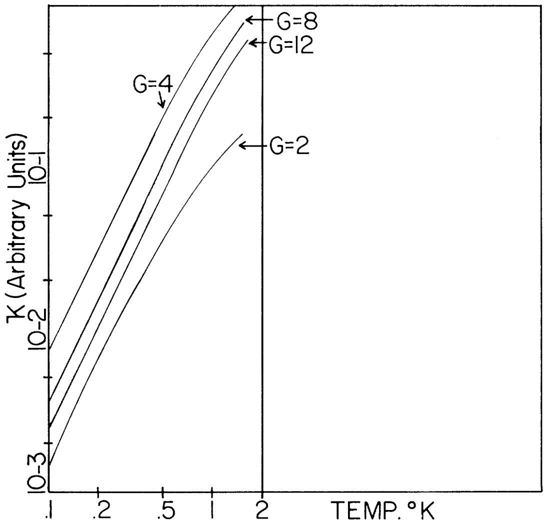

FIG. 2. Temperature dependence of the thermal conductivity, K, of glass vs the absolute temperature T on a log-log plot. The curve for $G=2$ has been displaced one decade downward in order to accomodate it more completely in the same figure. The slope of the straight-line sections of the various lines is 2.0. Note that increasing G moves the beginning of the bend in the curve to higher temperatures. Increasing G implies increasing the number of traps.

I have plotted the temperature dependence of Eq. (7) in Fig. 2 using G and δ as parameters.

All the slopes below 1°K are very close to 2 in contrast to the experimental values, which are slightly less than 2. This discrepancy could be due to the fact that I have assumed a constant collision distance, l, assuming that the traps themselves are the scatterers. It is very possible that l decreases with an increase in temperature due to additional scattering from phonons and free excitations. With a 30% decrease in l in the range 0.1–1°K, the slopes in Fig. 2 would be 1.85. The larger G is, the higher is the temperature at which the bending in Fig. 2 occurs. This bending is also characteristic of the experimental thermal conductivity. It represents the point at which the rate of evaporation of excitations from the traps decreases because of depletion and the gas of excitations tends toward a conductivity proportional to $T^{1/2}$, in this approximation. Before this conductivity is reached the excitations are "thermally unlocked" and the thermal description is then given by the material in the first part of this paper.

The temperature dependence of C_P is $T^{3/2}$, which one obtains in the standard way by dividing the thermal conductivity by the thermal speed which goes as $T^{1/2}$. The $T^{3/2}$ compares favorably with the results for glass given by Zeller and Pohl[1] where I measure $T^{1.44}$ from their Fig. 10.

All that is required is the existence of at least one bound state for the "locked-in" excitations. Without this, Eq. (4) would be invalid. In Fig. 2 I use $\delta = 0.1$°K but 0.05°K works equally well. It is apparent that the well has to be deep enough to localize the excitation and it may be that the well may actually have several bound states. I have used the simplest (one bound state) case for illustrative purposes. Evaluating the constants I find that $l \simeq 0.1$ cm for germania at $T = 0.1$°K ($G=12$, $\delta = 0.1$°K, $T_L = 3$°K) in order that the value calculated for the thermal conductivity agree with experiments. ($K \sim 5\times10^{-6}$ W cm^{-1} °K^{-1} at 0.1°K.[1]) This value of l is considerably greater than the distance between traps (~ 5 Å) that would exist if essentially all atom sites (germanium sites, in this case) were traps. Because of the shallowness of the traps the "size" of the scattering center would be quite small and the value of $l \simeq 0.1$ cm may not be out of line for this assumed primary scattering mechanism.

In addition, recent results of Golding, Graebner, and Schute[13] on the saturation of ultrasonic absorption are explainable by the existence of the shallow traps. If at low ultrasonic intensities the primary absorption is by excitations being released from the traps, then at higher intensities the absorption would decrease as the number of excitations in shallow traps would be diminished by the presence of the higher intensity ultrasound. This is not too different an explanation from the saturation of the two-level system given in Ref. 13.

The value of m^* calculated from the value of K is $m^* = 4.6\times10^{-25}$ g. This is considerably less than the mass of a germanium atom (12×10^{-23} g). The fact that the vitreous germania has a negative expansion coefficient at these temperatures suggests that the excitations are actually localized higher density regions in germania.

I further suggest that glasses, greases, and waxes have no first-order liquid-solid transitions, because the excitation formation energy is less than the $k\theta_D$, where θ_D is the Debye temperature. In this case there is no energy gap between the top of the Debye spectrum and the bottom of the excitation spectrum. Substances with a first-order liquid-solid transition indeed seem to possess a gap between these two energies. In the case of vitreous germania $\theta_D = 309$°K and T_V

=20.5°K, and therefore germania possesses no first-order liquid-solid transition.

In summary, this excitation representation seems to explain the high-temperature (3–50°K) behavior better than does the Debye model. Below 1°K it is possible that "locked-in" excitations play an essential role in determining the thermal properties of the glass. Not only does Fig. 2 give a slope close to the experimental slope, but it also exhibits the bending attribute shown by the experimental results (beginning at about 1°K). This bending is proposed to be due to thermal saturation similar to the ultrasonic saturation of Golding. The existence of traps that bind an excitation is essential in this treatment. Experimentally one could check the hypothesis of "locked-in" excitations by cooling very slowly between 5 and 1°K on the way down to lower temperatures. Presumably this would lower the number of "locked-in" excitations and reduce the low-temperature specific heat (between 0.1 and 1°K), as well as the thermal conductivity.

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