PHYSICAL REVIEW B VOLUME 8, NUMBER 6 15 SEPTEMBER 1973

Low-Temperature Specific Heat and Thermal Conductivity of Noncrystalline Dielectric Solids*

R. B. Stephens

Laboratory for Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 2 April 1973)

The specific heat and thermal conductivity of amorphous As_2S_3, B_2O_3, $3SiO_2 \cdot Na_2O$, $CaK(NO_3)_3$, GeO_2, and GE No. 7031 varnish has been measured between 0.05 and 2 K. Their properties were found to be very similar to those of the previously measured glasses: SiO_2, Corning code 7740, BeF_2, Se, polymethylmethacrylate (PMMA), polystyrene (PS), Lexan, and glycerol. They all have a specific heat $C_v = c_1 T + c_3 T^3$, where c_1 varies from 7 to 50 erg/g K, and c_3 from 1.2 to $3c_{\text{Deb}}$, depending on the material (c_{Deb} is the coefficient calculated with the Debye model). They also all have a conductivity, for $T \overset{\sim}{<} 0.5$ K, of $\kappa = \beta(T/\alpha)^\delta$ where β varies from 1.6 to 16 W/cm K, the exponent δ spans the range 1.9 ± 0.1, and $\alpha = 1$ K. This uniformity of thermal properties among the diverse group of glasses measured is as difficult to explain as their temperature dependence, and is so far not understood.

I. INTRODUCTION

The low-temperature thermal properties of crystalline dielectrics, both pure and impure, are well understood. The specific heat C_v of pure crystals, obeys the Debye law

$$C_v = c_3 T^3 \tag{1}$$

at temperatures below $10^{-2}\Theta$, where Θ is the Debye temperature. c_3 usually agrees to within a few percent with the Debye prediction c_{Deb} computed from experimental sound velocities[1]:

$$c_{\text{Deb}} = \frac{2\pi^2}{5}\,\frac{k_B^4}{\hbar^3 \rho v_{\text{Deb}}^3} = 4.068 \times 10^{17}\left(\frac{\text{erg}}{\text{sec}^3\,\text{K}^4}\right) \times \rho^{-1}\left(\left\langle \frac{1}{v_l^3}\right\rangle + 2\left\langle \frac{1}{v_t^3}\right\rangle\right) = 234\,\frac{Nk_B}{\rho\Theta^3}\,, \tag{2}$$

where v_l and v_t are the longitudinal and transverse speeds of sound, v_{Deb} is the appropriate average of v_l and v_t, N is the number density of atoms, ρ is the mass density, and k_B is Boltzmann's constant. In impure crystals, the specific heat can be considerably larger if the defects have states of low excitation energy (Schottky anomalies).[1]

The low-temperature thermal conductivity of pure crystalline dielectrics is well described by the Casimir model of phonon scattering by the crystal surfaces. Impurities in crystals can lower the conductivity by many orders of magnitude. This is usually described as phonon scattering by lattice defects,[1] and is well accounted for by various models (isotope effect, resonant scattering, etc.).

The situation is much less satisfactory, however, in noncrystalline solids. It has been known for some time that a substance in its glassy phase has a larger specific heat than in its crystalline phase at all but the highest temperatures. Such a difference cannot be explained, on the basis of the Debye model, by the different sound velocities (see Refs. 29–41 in Zeller and Pohl[2]). It has recently been observed that the Debye model cannot describe the specific heat of glasses even at temperatures as low as $10^{-3}\Theta$. Below $10^{-2}\Theta$ [Θ defined through Eq. (2)], the specific heats of vitreous SiO_2, GeO_2, Se, polymethylmethacrylate (PMMA), and polystyrene (PS), were found to be dominated by a term linear in temperature.[2,3] This linear term appeared to be independent of accidental impurities, as demonstrated for SiO_2.[2] Also, in contrast to crystalline solids, noncrystalline solids were found to have thermal conductivities which were not only similar in magnitude, but also in temperature dependence. At low temperatures ($T < 10^{-2}\Theta$), the conductivity κ follows a power law

$$\kappa = \beta(T/\alpha)^\delta\,, \tag{3}$$

where $\alpha = 1$ K and δ was determined to be ≈ 1.8 for all substances studied, namely, SiO_2, GeO_2, Se, sodium borosilicate glasses (Pyrex), and the polymers PMMA and PS.[2,3]

This work, together with the earlier work on noncrystalline solids referred to in Ref. 2 (hereafter I) led to the suggestion that the linear specific-heat anomaly, and the thermal conductivity varying as the 1.8th power of T, might be characteristic of the noncrystalline state. This we wanted to test. We anticipate our conclusion: We have increased the number of different noncrystalline solids investigated to date from 6 to 13, and all of them show the same anomalous thermal behavior described above.

II. EXPERIMENTAL METHODS

Specific heat and thermal conductivity were measured in the same cryostat, and by the same

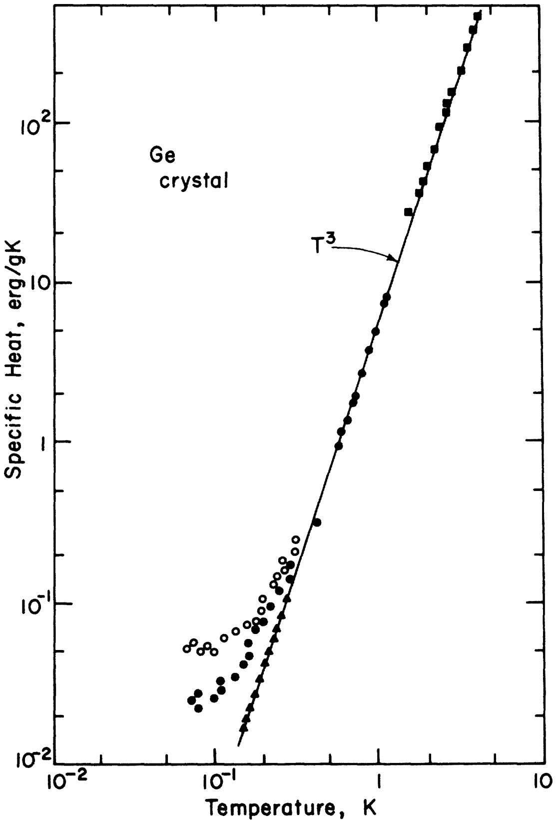

FIG. 1. Specific heat of crystal Ge. The solid line is the Debye specific heat. The data points above 1 K (■) are after Keesom and Pearlman (Ref. 6). The full circles and the open circles are our measurements of a 164-g Ge crystal with one and two thermometers, respectively (Ref. 8). The triangles show the data corrected for the heat capacity of the addenda.

techniques as described in I. Great care was taken to recalibrate the germanium thermometer, a secondary temperature standard in the demagnetization cryostat, against the susceptibility of cerium magnesium nitrate, our primary standard.[4] The first indication that the Ge-thermometer calibration had changed slightly since the original calibration[4] appeared in measurements of the thermal conductivity of a Li^7 F crystal, used as a reference in our laboratory. Below 0.2 K, the conductivity was found to deviate from the Casimir T^3 behavior observed earlier on the same sample.[4] After recalibration (which changed temperatures by < 5%), we were able to reproduce Harrison's data.[4] In particular, the exponent of the temperature dependence was within 0.1% of 3. As an additional test of our equipment, we measured the specific heat of a high-purity Ge crystal,[5] provided by Hall of the General Electric Company. As can be seen from Figs. 1 and 2, our results agree with extrapolations of the earlier, higher-temperature measurements,[6] to 0.5 K. Below 0.5 K, the specific heat deviated from T^3 (the full circles in Fig. 1). We suspected that this excess specific heat resulted from the heat capacity of our addenda, which with our technique is predominately the carbon in our working thermometer. We mounted a second carbon resistance thermometer on our sample, remeasured the specific heat[8] (the open circles in Fig. 1), and found that it had indeed increased. The difference between the two heat capacities (the product of specific heat and sample mass) is the heat capacity of the second thermometer, shown in Fig. 3. Assuming that the specific heats of the two thermometers are identical, one can compute the heat capacity of the first thermometer, and subtract it from the measured heat capacity to obtain the specific heat of the Ge crystal alone, as shown by the triangles in Fig. 1. The result agrees well with the expected Ge specific heat all the way down to 0.15 K. Below that temperature, the addenda correction is so large that the uncertainty becomes larger than the corrected heat capacity.

The large heat capacity of our working thermometers was surprising. They are mostly carbon, and previous measurements on pure graphite[9] indicated that they should have the heat capacity shown by the lowest line in Fig. 3. The measured heat capacity of our thermometer is actually an order of magnitude higher, but our measurements and measurements of carbon resistors by Keesom

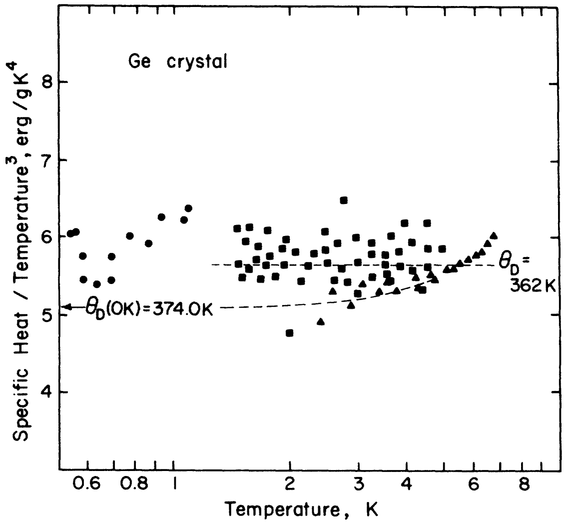

FIG. 2. Specific heat of crystal Ge presented as C/T^3 vs T. The square data points are after Keesom and Pearlman, the triangular points are after Flubacher *et al.* (Ref. 6). The dashed lines are the fits to their data. The arrow indicates C/T^3 as determined from elastic constants by De Launay for 0 K (Ref. 7). The full circles are our data for $T > 0.5$ K.

et al.[10] extrapolated from $T > 1.2$ K are consistent with each other. The fact that the carbon in resistors is mixed with clay to produce the proper resistivity may be the cause of the difference.

Our results help to explain the previous measurements of nominally pure rubidium bromide and quartz crystals by Zeller and Pohl.[2] They found excess heat capacities of approximately the same size as we found above (see Fig. 3). The excesses were ascribed to some unknown impurities at the time, but it now appears that the excesses are due to the carbon thermometers.

For the purposes of this paper, heat capacities of the working thermometers present no problem. Even the smallest of our glass samples had a heat capacity $C > 40$ erg/K, larger by an order of magnitude than that of our thermometers.

As one can see from Eq. (2), the specific heat in the Debye model is completely determined by the sound velocities and the mass density. For $CaK(NO_3)_3$, these quantities were unknown, and neither was the sound velocity known for $3SiO_2 \cdot Na_2O$.

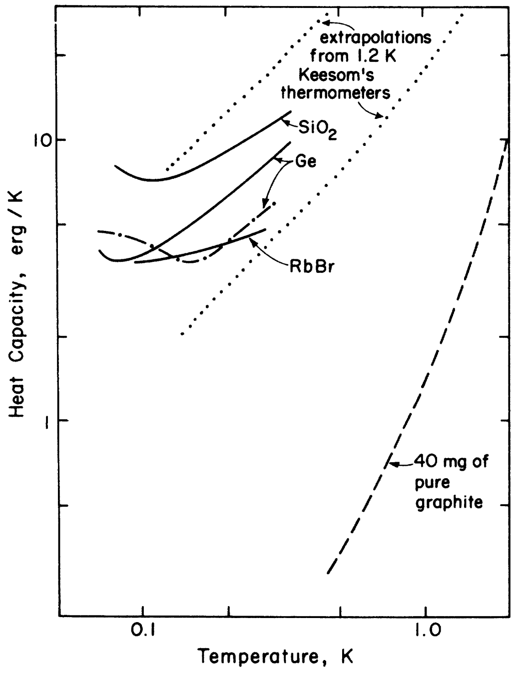

FIG. 3. Heat capacity of carbon resistance thermometers. The dash-dot line is the measured heat capacity of the second carbon thermometer on the Ge crystal. The solid lines are the excess heat capacities obtained by subtracting the expected Debye heat capacity from the measured heat capacity for three crystals measured in our cryostat: SiO_2, RbBr, and Ge. The dotted lines are extrapolations from 1.2 K after measurements by Keesom *et al.* (Ref. 10) on carbon resistance thermometers. The lowest line (dashed) is the heat capacity predicted if the 40-mg thermometer on the Ge crystal were pure graphite, after van der Hoeven and Keesom (Ref. 9).

The density of the nitrate glass was determined by comparing its weight in air and in paraffin oil, rather than in water because this glass is very hygroscopic.

For the velocity measurements, we used cylindrical samples 1–2-cm long and 1 cm in diameter, with the ends polished flat and parallel to within several wavelengths of visible light. This is a very good optical polish for the acoustic sound wavelength of ~0.05 cm used for our measurements. Again, particular care had to be taken with the $CaK(NO_3)_3$ sample, so it was polished with grit suspended in kerosene (rather than water or alcohol), and then covered with a layer of vacuum grease.

A 10-MHz quartz transducer (*X* cut for transverse or AC cut for longitudinal waves) was bonded to one end with dust-free Pentene at ~ 100 K. The sample was then cooled to ~ 4 K, and pulsed with 1-μsec, 10-MHz pulses. The time of arrival of the echoes was determined to within 0.1% using the trigger delay on an oscilloscope, but because of uncertainty in the thermal contraction, the final v_{Deb} was limited to a 1% accuracy.[11]

III. SAMPLE PREPARATION

For these investigations, we prepared samples of As_2S_3, $CaK(NO_3)_3$, B_2O_3, and GE No. 7031 varnish. Glasses are much less difficult to produce than crystals, but one still needs to take some precautions as listed below.

The As_2S_3 starting material[12] was stated to have < 10-ppm heavy-metal impurities. It is, however, hygroscopic, so the principal contaminant is probably water. The powder was heated in a silica tube to 100 °C in vacuum for 24 h to drive off water vapor. Then the tube was sealed, heated to 500 °C, held there for ~ 6 h, and cooled in air to produce a dark red solid with a metallic sheen, but full of bubbles—the bubbles were probably a result of residual water. One sample, provided by Leadbetter was almost bubble free.

The $CaK(NO_3)_3$ was produced from equimolar amounts of analytic-research-grade KNO_3, and $Ca(NO_3)_2 \cdot 4H_2O$.[13] It was heated in air in a Pyrex beaker until the mixture dissolved into its own water of hydration, boiled until viscous, and poured into an aluminum-foil mold which was sitting in water. If enough water was driven off, the melt solidified to produce a rather plastic clear material. Since we did not know how much water remained, or whether it would affect our C_v results, we repeated our procedure to produce another sample, and presumed that we would end up with different amounts of water in each. These samples were too soft to polish for sound velocity measurements.

A harder sample was prepared by extending the boiling time. After more water was driven off, a white precipitate formed which redissolved upon further heating.[14] One cannot heat much beyond this point, since the NO_3^- starts to break down with the emission of brown fumes. If one is very careful about avoiding nucleation centers, the melt can then be cooled without crystallization. During cooling, the solid contracts and breaks the Pyrex beaker, but usually the sample remains intact. We used one of these harder samples to determine v_{Deb}.

The B_2O_3 was prepared from analtyic-research-grade boric acid. It was dehydrated overnight in vacuum at 200 °C. The caked powder was then broken up and transferred into a thin platinum crucible. It was gradually heated in vacuum to 670 °C, held there for 24 h, and cooled by turning off the oven. The platinum could be easily peeled off the clear bubble-free sample.

To obtain the varnish sample, we filled a loosely covered cardboard box with Ge No. 7031 varnish and set it aside for several months. The cardboard allowed the varnish to dry from all sides, and the closed box made the varnish dry slowly enough to prevent bubble formation. The result was a sample with the consistency of gum rubber.

IV. EXPERIMENTAL RESULTS

A. Specific Heat

The specific heat observed on $3SiO_2 \cdot Na_2O$ (soda-silica), As_2S_3, B_2O_3, and $CaK(NO_3)_3$ has the same characteristic temperature dependence observed previously in other glasses. The data are well fitted by

$$C = c_1 T + c_3 T^3, \qquad (4)$$

and are shown as C/T vs T^2 in Fig. 4. c_1 varies from 7 to 50 erg/g K. In addition, c_3 is considerably larger (by 20–200%) than one would calculate from acoustic measurements. This is something which was not stressed earlier—not only is there a linear term which is not predicted by the Debye model, but the cubic term is substantially larger than predicted by the Debye model.

It is important to know whether the specific heat we measure is well described by Eq. (4), or whether the fit can be improved by using a more complicated power series. To test this, we tried a variety of fits to the data, between 0.1 and 2.0 K, for several of our glasses. It was found, for example, that SiO_2 can be represented in the following ways:

$$\begin{aligned} C_v(\text{erg/g K}) &= 12T + 17.5T^3, && \text{rms} = 0.082 \\ &= 10.7T + 7.4T^2 + 12.8T^3, && \text{rms} = 0.076 \\ &= 9.9T + 14.8T^2 - 3.2T^3 + 10.3T^4 - 1.9T^5, && \text{rms} = 0.077 \end{aligned}$$

where T is measured in °K and the rms is the root-mean-square fractional deviation of the data from the fits. PMMA can be equally well described with the following polynomials:

$$\begin{aligned} C_v(\text{erg/g K}) &= 47.7T + 292T^3, && \text{rms} = 0.052 \\ &= 36.9T + 73T^2 + 208T^3, && \text{rms} = 0.039 \\ &= -5.4T + 562T^2 - 1607T^3 + 2610T^4 - 1263T^5, && \text{rms} = 0.032 \end{aligned}$$

and finally, Se can be represented by

$$\begin{aligned} C_v(\text{erg/g K}) &= 7.92T + 190T^3 + 31.0T^5, && \text{rms} = 0.044 \\ &= 8.34T - 3.2T^2 + 194T^3 + 29.6T^5, && \text{rms} = 0.044 \\ &= 5.21T + 3.30T^2 + 73T^3 + 143T^4 - 24.7T^5, && \text{rms} = 0.043. \end{aligned}$$

One can see that we gain little information by fitting the data with five parameters. Although the data are fitted somewhat better, the size of the individual components have very little significance. The two- and three-parameter fits are shown graphically in Fig. 5. First, one can see that our two-parameter curves give good fits, which more parameters do not greatly improve (see also the value of rms shown above), and second, for the three-parameter fit, the T^2 term is rather small compared to the other two components at all temperatures—it is not much larger than the scatter in our data. We therefore conclude that Eq. (4) describes the data well, but the presence of a small T^2 term cannot be ruled out.

Impurities in glasses, just as in crystals, can obscure the intrinsic specific heat.[15] The effect of a common impurity such as iron in borosilicate glass is shown in Fig. 6; the iron spins produce a rather broad anomaly in the specific heat. One can see

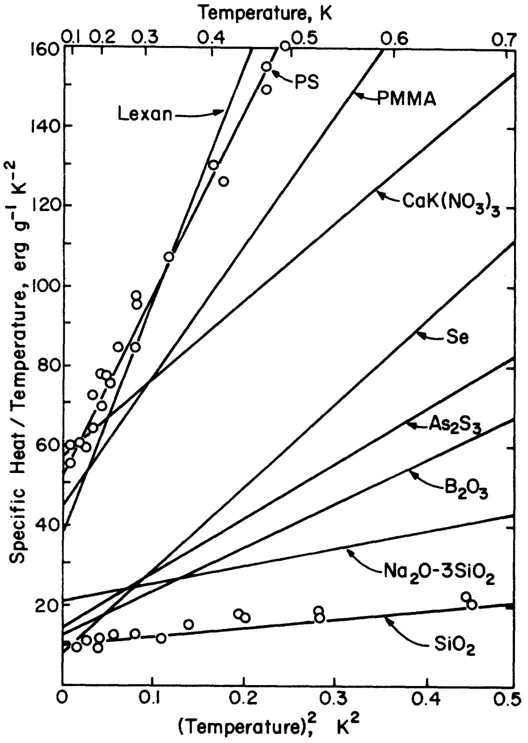

FIG. 4. Specific heat of noncrystalline solids plotted as C/T vs T^2. Partly for the sake of completeness, and partly because of minor changes in the earlier results caused by the recalibration of our temperature standard, we include the corrected results obtained previously. The data on Se and SiO_2 are after I. The data on PS (polystyrene) and PMMA (polymethylmethacrylate—plexiglass) are after Stephens *et al.* (Ref. 3). The data on Lexan are after G. L. Salinger and G. S. Cieloszyk (private communication). The intercept with the vertical axis determines the linear component of the specific heat; the slope of the straight line determines the T^3 term. The masses of the samples we measured were soda-silica, 62.3 g; As_2S_3, 25.6 g; B_2O_3, 34.6 g; $CaK(NO_3)_3$, 54 g.

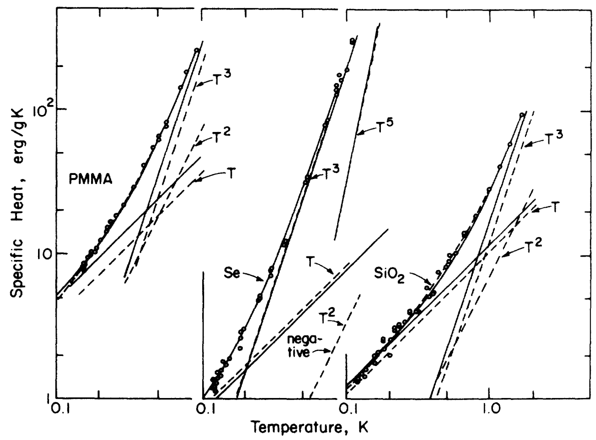

FIG. 5. Polynomial fits to specific-heat data for SiO_2, Se, and PMMA. The solid lines are the components and sum of the fit $C_v = c_1T + c_3T^3$. The dotted lines are the components and sum of the fit $C_v = C_1T + c_2T^2 + c_3T^3$. The Se data need, in addition, a T^5 component, but that is negligible below 0.8 K. One can see that the differences between the fits are within the scatter of the data.

similar sample-dependent effects in several of the glasses we have measured, although the impurities causing these changes in the specific heat have not yet been identified. Figure 7 shows the three samples of As_2S_3 which we measured. Two of the samples were made in our laboratory, with successively more care to remove water, and the purest was supplied by Leadbetter. The specific heat of his sample is well described by Eq. (4); the others seem to have significant concentrations of impurities. Reproducible results are the best indication that one is observing an intrinsic effect. For instance, the two samples of $CaK(NO_3)_3$ we measured presumably had different concentrations of water, but we found they had the same specific heat within the scatter of the data. There would presumably be different impurity levels in samples made in different laboratories. Figure 8 compares the specific heat of amorphous Se measured at Grenoble[16] and at Cornell.[2] The French measurements were not well fitted by Eq. (4) and showed a somewhat higher specific heat than ours. Las-

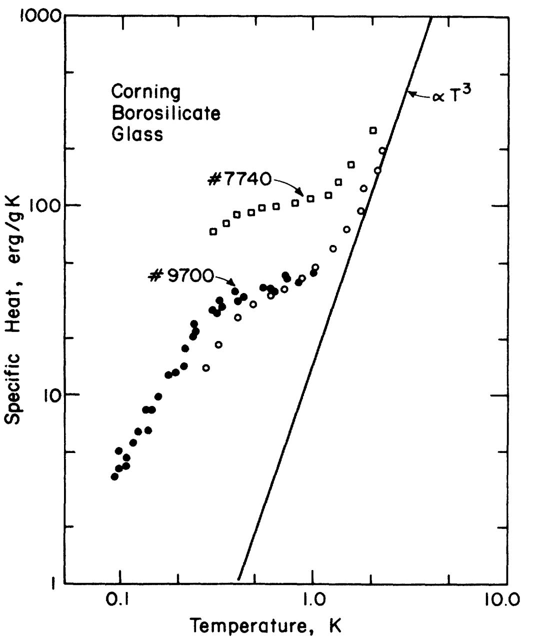

FIG. 6. Specific heat of Corning borosilicate glass Nos. 9700 and 7740. The open circles and squares are after I, the full circles are our data. The solid line is included as a reference αT^3 line. The size of the anomalies are roughly what would be expected from the measured concentration of iron in these glasses: 100 ppm for 7740 and 12 ppm for 9700 (Ref. 2).

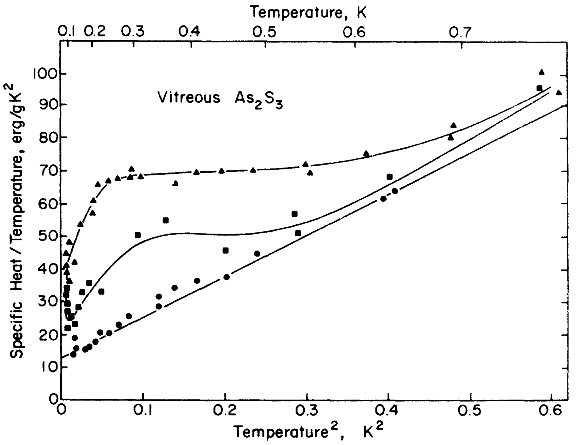

FIG. 7. Specific heat of three As_2S_3 samples plotted as C/T vs T^2. The two upper curves are from samples which were produced by us with successively more care to remove water. If one assumes that the differences between them and the lowest curve are due to two-level systems, one can calculate the density of these systems to be 68×10^{16} cm^{-3} for the upper curve, and 26×10^{16} cm^{-3} for the lower one. The lowest curve is from a sample which was supplied by Leadbetter.

jaunias has since measured a more carefully quenched sample, and his new data (unpublished) agree with ours to within the experimental error.[17]

Table I presents our results in compact form. The theoretical specific heat predicted by the Debye model is shown in column 6. It was determined by speed of sound measurements; the average velocity, $v_{\rm Deb} = (1/v_l^3 + 2/v_t^3)^{-1/3}$, is shown in column 4. The parameters of our fit to the experimental specific-heat data are shown in columns 7 and 8. One can see, by comparing $c_{\rm Deb}$ and c_3, that there is little relation between the Debye prediction and the experimental values for any glass. Worse, the differences from the Debye predictions, c_1 and c_3-$c_{\rm Deb}$, seem to vary randomly over a factor of 10 for the different glasses, and this variation remains about the same whether one uses g atom, g mole (a rather arbitrary concept in glasses), or cm^3 as units in the calculations.

We include columns 9–11 to give a feeling for the size of these anomalous results. The Debye model predicts a phonon density of states:

$$\frac{\partial n(\hbar\omega)}{\partial(\hbar\omega)} = \frac{3(\hbar\omega)^2}{2\pi^2\hbar^3 v_{\rm Deb}^3}$$

$$= \frac{15\rho c_{\rm Deb}(\hbar\omega)^2}{4\pi^4 k_B^4} = b_{\rm Deb}(\hbar\omega)^2 . \qquad (5)$$

The observed specific heat indicates a larger density of states

$$\frac{\partial n(\hbar\omega)}{\partial(\hbar\omega)} = a + (b + b_{\rm Deb})(\hbar\omega)^2 , \qquad (6)$$

where we have chosen to keep the Debye phonon density of states separate. The connection between c_1 and a, and between c_3 and b can be worked out for specific models. One finds the relations

$$a = \alpha\rho c_1/\pi^2 k_B^2 , \qquad (7)$$

$$b = (\gamma\rho/\pi^4 k_B^4)(c_3 - c_{\rm Deb}) , \qquad (8)$$

where the constants α and γ depend only slightly on the model. $\alpha = 6$ and $\gamma = \frac{30}{7} \approx 4.3$ for two-level systems, $\alpha = 3$ and $\gamma = \frac{15}{4} \approx 3.8$ for harmonic oscillators (infinite-level systems), and α and γ are intermediate for intermediate numbers of levels. The comparison between the Debye density of states and the measured density of states is shown in Fig. 9, where we plot $[\partial n(\hbar\omega)/\partial(\hbar\omega)]_{\rm Deb}$ and $[\partial n(\hbar\omega)/\partial(\hbar\omega)]_{\rm Spec\ Ht}$ for SiO_2. The excess systems were assumed to be harmonic oscillators, just as are Debye phonons. Note especially that although the excess is most noticeable in the specific heat at 0.1 K, the absolute difference in $[\partial n(\hbar\omega)/\partial(\hbar\omega)]$ is largest at high temperatures. One does not get a realistic idea of the number of systems involved by looking at the linear specific-heat term alone; one may get a better feeling of the number of systems involved at any temperature T by integrating over all the excess density up to $3T$.[18] The integral up to 1 K (the number of oscillators involved in the specific heat at 0.3 K) is presented as n in column 11. One can see that this n is remarkably constant, $n \sim 10^{17}$ cm^{-3} or 20–200$\times 10^{-6}$ oscillators per atom in the glass.

B. Thermal Conductivity

The thermal conductivity measurements are presented in Fig. 10. The recalibration of our Ge thermometer changed the range of the exponent

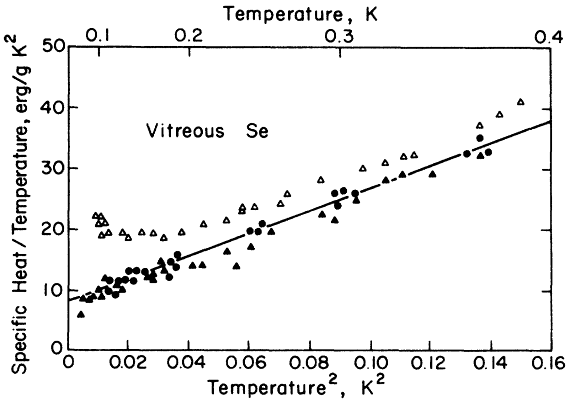

FIG. 8. Specific heat of Se glass plotted as C/T vs T^2. The full circles are our data. The open triangles are after Lasjaunias *et al.* (Ref. 16); they have since measured a more carefully made sample, indicated by the solid triangles, and their data now coincide with our data (Ref. 17).

TABLE I. Summary of the data available on low-temperature specific heat and thermal conductivity of noncrystalline solids. The first four columns give some general parameters of the materials studied. Columns 5 and 6 pertain to the Debye model; the Debye temperature in column 5 is based on the atomic (not the molecular) number density. Columns 7 and 8 contain the parameters to Eq. (4) which were used to fit our specific-heat data. Note that these numbers bear very little resemblance to the coefficient c_{Deb} predicted by the Debye model (in column 6). Columns 9 and 10 are the coefficients of Eq. (6), which describes the excess density of excitations calculated under the assumption that they are harmonic oscillators. The numbers one calculated depend on the exact model used; for details see the text. n, in column 11, is the integral of these oscillator states, up to 1 K; they are the states which would be involved in the specific heat at 0.3 K. Columns 12 and 13 are the parameters for Eq. (3). This equation describes the data well up to 0.4–1 K (depending on the substance). Column 14 is the Debye phonon relaxation time at 0.3 K from Eq. (9).

Material[a]	1 Mass dens. (g/cm^3)	2 Avg. At. wt.	3 Avg. Mol. wt.	4 v_{Deb} (10^5 cm/sec)	5 Θ_{Deb} (K)	6 c_{Deb} (erg/g K^4)	7 c_1 (erg/g K^2)	8 c_3 (erg/g K^4)	9 a (10^{32} erg^{-1} cm^{-3})	10 b (10^{64} erg^{-3} cm^{-3})	11 n (10^{16} cm^{-3})	12 β (10^{-4} W/cm K)	13 δ	14 τ (10^{-9} sec)
SiO_2	2.2[b]	20.	60.[c]	4.1[d]	492.	8.1	11.	20.	3.9	0.28	5.6	2.4	1.87	9.6
$3SiO_2 \cdot Na_2O$	2.4[b]	20.	61.[c]	3.56	438.	11.2	20.	34.	7.7	0.57	11.	1.7	1.92	5.2
Corning code No. 7740	2.2[b]	20.	...	3.65	454.	11.3	~10.[e]	22.[e]	3.6	0.25	5.1	2.1	1.92	6.9
GeO_2	3.6[b]	35.	105.[c]	2.6	306.	19.5	9.	26.	5.2	0.23	7.4	3.7	1.91	8.7
As_2S_3	3.2[b]	49.	246.[c]	1.69[f]	170.	78.5	14.	130.	7.0	1.9	11.	17.	1.92	24.
B_2O_3	1.8[b]	14.	70.[c]	2.04	259	78.[f]	13.	110.	3.8	0.53	5.7	3.5	1.96	4.9
BeF_2	2.0[b]	16.	47.[c]	3.02	380.	22.2	...[g]	44.	...	...	...	...	...	...
Se	4.3[b]	79.	79.[c]	1.30[f]	123.	170.[f]	7.5	190.	5.0	0.89	7.7	7.9	1.81	7.3
PMMA	1.2[b]	6.5	104.[c]	1.79	254.	182.	46.	290.	8.7	1.3	13.	3.3	1.81	5.6
PS	1.0[b]	6.7	100.[c]	1.67	224.	255.	51.	450.	8.4	2.2	14.	2.0	1.87	3.0
Lexan[h]	1.2[b]	7.4	238.[c]	1.53	209.	285.	38.	410.	7.2	1.6	11.	~2.	...	3.8
$CaK(NO_3)_3$	2.1[b]	20.	217.[c]	1.94	232.	78.8	56.	120.	19.	1.1	27.	1.6	1.90	1.4
glycerol	1.3[b]	6.6	92.[c]	...	...	...	~20.[i]	110.[i]	...	...	...	...	...	...
Ge No. 7031 varnish	1.09[b]	...	...	...	...	...	64.5	193.	...	...	...	5.4	1.87	...

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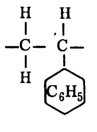
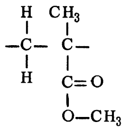
[a] For a description of the samples we did not produce, see the following references: for SiO_2, Corning code No. 7740, GeO_2, and Se, Ref. 2; for PMMA and PS, Ref. 3; for BeF_2, K. E. Wycherley, Ph.D. thesis (University of Bristol, 1969) (unpublished); for glycerol, R. S. Craig, C. W. Massena, and P. M. Mallya, J. Appl. Phys. 36, 108 (1965).

[b] The mass densities were obtained from a variety of sources; for the SiO_2, GeO_2, BeF_2, Se, glycerol, see I. Gutsow, Z. Phys. Chem. 221, 153 (1962); for the Corning glass, see the Corning catalog; the density of the B_2O_3 is from CRC tables; the density of the polymers was measured by G. L. Salinger and G. S. Cieloszyk; the density of the As_2S_3 is from F. J. DiSalvo (private communication), and we measured the density of the $CaK(NO_3)_3$.

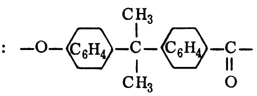
[c] The molecular mass is based on units in the crystalline phase of these glasses. For the polymers, the units are taken to be

PS:  ;

PMMA: 

$$-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}_3}{\underset{\text{C=O}-\text{O}-\text{CH}_3}{\text{C}}}-$$

;

Lexan: 

[d] O. L. Anderson, Phys. Chem. Solid 12, 41 (1959).

[e] From measurements in 90-kG field and $T > 1.2$ K; see R. A. Fisher, G. E. Brodale, E. W. Hornung, and W. F. Giauque, Rev. Sci. Instrum. 39, 108 (1968).

[f] C. R. Kurkjian (private communication).

[g] Wycherley's data only go down to 1.2 K; this is not low enough to determine the existence of a linear component.

[h] These are unpublished results by G. L. Salinger and G. S. Cieloszyk. The measurements were made down to 0.4 K; this was not low enough to determine the low-temperature dependence of the conductivity.

[i] Fit from extrapolation of $T > 1.2$ K data by Craig *et al.*, see Ref. a.

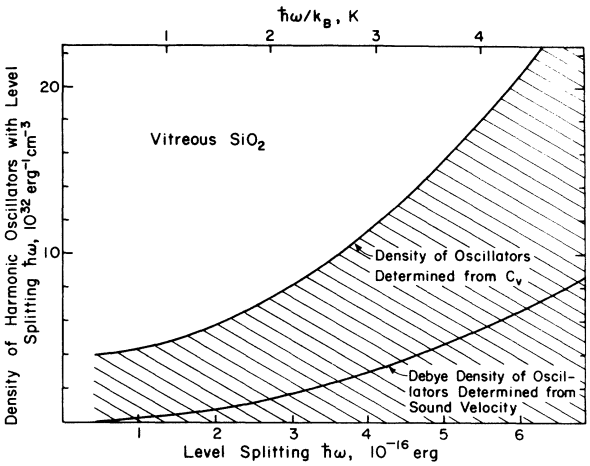


FIG. 9. $[\partial n(\hbar\omega)/\partial(\hbar\omega)]_{\rm Deb}$ and $[\partial n(\hbar\omega)/\partial(\hbar\omega)]_{\rm Spec\ Ht}$ vs $\hbar\omega$ for SiO_2 glass, assuming that the excess states are harmonic oscillators. Harmonic oscillators are frozen out roughly at $\epsilon/k_BT=\frac{1}{3}$, so, for instance, all the states up to $\epsilon/k_B=1$ K are involved in the specific heat at 0.3 K. If one were to assume that the extra specific heat was caused by two-level systems instead of harmonic oscillators, the excess density of states would be roughly doubled; see text.

δ in Eq. (3) by about 5% from 1.8 ± 0.1 to 1.9 ± 0.1. Otherwise, the previously published data are substantially unchanged; the new measurements on soda-silica, GeO_2, As_2S_3, B_2O_3, $CaK(NO_3)_3$, and GE No. 7031 varnish are very similar to the results obtained for the other glasses. β and δ from Eq. (3) are shown in columns 12 and 13 of Table I. In the Debye model, one can estimate the phonon scattering from

$$\kappa=\tfrac{1}{3}C_v v_{\rm Deb}^2\tau,\quad \tau=\frac{3\kappa}{C_v v_{\rm Deb}^2}\ . \tag{9}$$

$C_v=c_{\rm Deb}T^3$ is the specific heat of the Debye phonons calculated from acoustic measurements, and τ is the phonon relaxation time. One can calculate τ from C_v, $v_{\rm Deb}$, and κ; τ is shown in column 14 of Table I for $T=0.3$ K.

V. DISCUSSION

A number of theories have been advanced to explain the linear term in the specific heat, as well as the anomalous thermal conductivity below 1 K. For a summary we refer the reader to Ref. 1; for detailed presentations we refer to the original papers.[19,20] These theories can be characterized according to two essentially different approaches. The first group[19] applies to glasses the concept of isolated active systems in an otherwise Debye-like matrix. These theories all depend on the presence of some kind of structure on the atomic level, giving rise to low-energy motional states of single atoms or molecules, or to electronic states. Such states have been seen many times in crystals, through specific heat as well as through phonon scattering. In particular, the latter effect is extremely sensitive to details of the surrounding lattice. There is, for instance, at least four orders of magnitude difference between the scattering strength of tunneling states of F^- ions in NaBr, and CN^- ions in KCl, although their effects on the specific heat are very similar.[21] It is not clear to us why the glass systems should be any less sensitive than crystals to the atomic structure around them. Since glasses at this level look very different (e.g., chains of divalent Se versus tetrahedra of SiO_4), it is difficult to understand the similarity of their behavior in the face of such divergence in crystals, and even more difficult to expect that any of these theories can be made to work for the variety of glasses observed.

The second group of theories[20] approaches the problem on a different scale. They explain the anomalous thermal effects using only the long-range disorder of glasses. This approach is perhaps more appealing in that it does not depend on the details of the atomic structure. But, for the same reason, it seems to be even more difficult to produce from these theories a prediction which can be tested experimentally.

The second group of theories, like the first group, makes the assumption that Debye plane-wave phonons carry the heat in glassy materials,

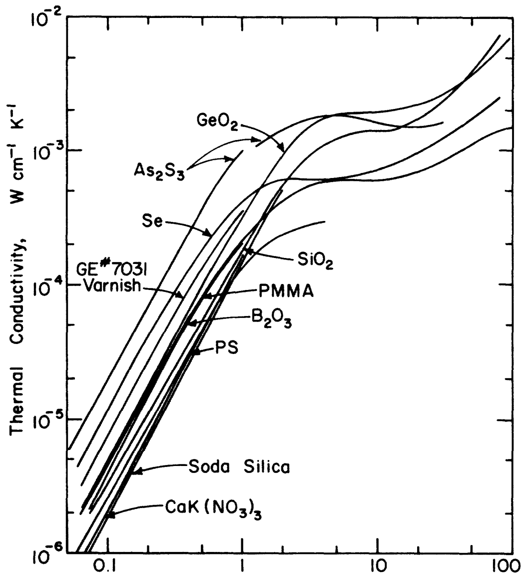


FIG. 10. Thermal conductivity of noncrystalline solids. The scatter in the data is comparable to the linewidth, so smooth lines are shown for all samples. The data on As_2S_3 above 1 K are after Leadbetter (private communications); those on Lexan are after Salinger and Cieloszyk (private communication).

and that the additional systems appearing in the specific heat act as scattering centers for the phonons, but do not carry heat themselves. As noted above, this assumption should lead to conductivities which are very sensitive to the structure of the glasses; the experimentally observed insensitivity of conductivity to different glass structures seems to present a difficult problem. As a result, we have begun to wonder whether the phonon picture is useful to describe heat transport in glasses, and would like to briefly mention our thoughts in the following.

Suppose the systems which show up in the specific heat are also involved in heat transport. Perhaps these systems are sufficiently numerous and extended in space, that they overlap and can transport energy between them without the mediation of the Debye phonons. At the same time, the Debye phonons are strongly scattered so they carry very little of the heat. Then the similarity of the conductivities follows from the similarity of the specific heats. This view implies that the quantities in the standard relation

$$\kappa = \tfrac{1}{3} C_v v l = \tfrac{1}{3} C_v l^2/\tau \qquad (10)$$

have to be defined to describe diffusion of heat among these systems. C_v is the specific heat of the systems, τ is the time needed to transfer heat between them, l, previously the phonon mean free path, is here the separation between the systems, and v is the ratio l/τ. Assuming that these systems must transfer energy with a velocity $v \lesssim v_{\mathrm{Deb}}$, one can calculate l. For silica one finds $l_{\mathrm{exp}} \geq 2\times 10^{-5}$ cm at 0.1 K. Since this mean free path is much shorter than the 0.2 mm in silica at 0.1 K predicted by the Debye model (see Fig. 9 in I), we can check our model by measuring the phonon mean free path directly.

In this laboratory, we are currently investigating two alternative ways of measuring the phonon mean free path. In one, we will check the Debye phonon model by looking for boundary-limited conductivity in thin glass fibers. According to the Casimir model, we should see boundary limited ($\kappa \propto T^3$) conductivities, instead of the observed bulk ($\kappa \propto T^{1.9}$) conductivities, in samples whose diameter is much smaller than the phonon mean free path. If no boundary effect in thin fibers is seen, then we can conclude that the Debye model is not applicable in glasses. In the other approach, Goubau is studying the propagation of heat pulses through very thin glass samples. One can construct a sample whose thickness is less than the Debye phonon mean free path at a reasonable temperature (i.e., 0.1 K). It might therefore be possible to make measurements starting at higher temperatures, and to observe changes in the heat-pulse diffusive profile as one goes into what the Debye model predicts as the ballistic regime. This approach can give us information on the speed as well as the mean free path of the thermal excitations in glass.

ACKNOWLEDGMENTS

I especially wish to thank Professor R. O. Pohl for his help and guidance throughout this investigation, and for many valuable suggestions and discussions. I also wish to thank G. S. Cieloszyk, G. L. Salinger, and J. C. Lasjaunias for permission to use their unpublished data. G. Schmidt and S. Camobreco of the Crystal Growing Laboratory of Cornell's Materials Science Center were of great help in advising and producing the glasses. A. J. Leadbetter, R. J. Ginther, and R. N. Hall were very kind to supply the samples that were used.

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*Work supported by the U.S. Atomic Energy Commission under Contract No. AT(11-1)-3151, Technical Report No. C00-3151-19 (unpublished). Additional support was received from the Advanced Research Projects Agency through the facilities of the Materials Science Center at Cornell University, Materials Science Center Report No. 1969 (unpublished).

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[10] Their resistors were 50-mg 1/10-W 10-Ω Allen-Bradley carbon resistors. See P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1347 (1957); and C. A. Bryant and P. H. Keesom, Phys. Rev. **124**, 698 (1961).

[11] For details, see Ph. D. thesis by Ber Chin Yap, Materials Science Center Report No. 1985. (Cornell University, 1973) (unpublished).

[12] "Ultrapure" powder from Alfa Inorganics, P. O. Box 159, Beverly, Mass. 01915.

[13] Recipe after C. A. Angell, J. Wong, and W. F. Edgell, J. Chem. Phys. **51**, 4519 (1969). For a review of other nitrate-based glasses, see L. G. van Uitert and W. H. Grodkiewicz, Mater. Res. Bull. **6**, 283 (1971).

[14] This effect was not mentioned in Ref. 13.

[15] For details see Ref. 2.

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