Thermal Conductivity of Borosilicate Glass*

M. P. Zaitlin† and A. C. Anderson
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 12 August 1974)

The thermal conductivity of a borosilicate glass has been measured in the temperature range 0.05–50 K. The samples contained well-defined holes to provide a source of phonon scattering. The results are consistent with the predictions of the Debye model using experimentally measured sound velocities. The results also indicate that thermal transport at temperatures below ≈ 30 K is provided by low-frequency phonons having a characteristic temperature $\lesssim 3$ K.

A great deal of data have been amassed on the thermal conductivity $\kappa(T)$ of amorphous dielectric materials.[1] The data have shown that despite the wide variance in the chemical makeup of these materials (polymers,[2,3] greases,[4] fused silica,[5] vitreous Se,[6] etc.) their thermal conductivities are remarkably similar both in magnitude and in temperature dependence. All amorphous materials have a plateau in the thermal conductivity (i.e., κ almost independent of temperature T) near $T \approx 10$ K and have κ approximately proportional to T^2 at lower temperatures.[2] Klemens[7] originally suggested that the plateau was due to the long mean free path of longitudinal phonons at and below 10 K. Since then, others have ascribed the plateau to resonant scattering of phonons by an unspecified mechanism at ≈10 K,[8] to "isotope" scattering by the amorphous structure,[2] and to short-range correlations in the amorphous structure.[9] These and other models[10] for the plateau have yet to be confirmed experimentally.

For lower temperatures ($T \lesssim 1$ K), Anderson, Halperin, and Varma[11] and Phillips[12] have developed a model for phonons resonantly scattering from two-state tunneling systems which gives $\kappa \propto T^2$ at low temperatures and also gives a contribution to the specific heat proportional to T as has been observed experimentally.[1] These tunneling systems can be saturated in ultrasonic measurements and give rise to an amplitude-dependent ultrasonic attenuation which has also been observed experimentally.[13-15] More recently, an anomalous temperature dependence of the sound velocity in fused silica has provided further evidence for this model.[16] However, it has yet to be determined experimentally to what extent the excitations which contribute to thermal conduction are related to the specific heat, or to a Debye density of states, in this low-temperature regime.

To explore the problems outlined above, we have measured the thermal conductivity of two different noncrystalline solids which contain well-defined cylindrical holes arranged perpendicular both to the surface of the material and to the flow of heat. These holes serve as an additional scattering mechanism for phonons. Knowing the mean free path of phonons due to boundary scattering by the holes, we get information on the specific heat of the phonons as well as on the phonon mean free path in the bulk material. Our results are consistent with the heat carriers being phonons with a density of states given by the Debye model using measured acoustic velocities. The results also indicate that the thermal conductance at temperatures up to ≈ 30 K is provided by low-frequency phonons having a characteristic temperature of $\lesssim 3$ K. It will be shown how this leads to the plateau discussed above.

If cylindrical holes are introduced in a solid, the heat that can flow for a given temperature gradient is reduced by two effects. First, there is a smaller volume for the heat to flow through because material has been removed. This is just a geometrical difference and is easily taken into account—the thermal conductivity of the material is unchanged. The second effect is the boundary scattering of phonons by the holes. This does give a reduction in the thermal conductivity because the phonon mean free path is shortened, and it was this mean free path which we wished to detect experimentally.

The measurements were made on 0.027-cm-thick, fused capillary arrays of borosilicate glass[17] and on 5–15-μm-thick polycarbonate sheets.[18] The samples of borosilicate glass all had approximately the same open area of ≈ 60% with hole diameters from 5 to 50 μm. The open area of the polycarbonate ranged from about 1 to 15% and the hole sizes varied from 0.1 to 8.0 μm. Hole size was uniform for a given sample.

The experimental arrangement for measuring κ

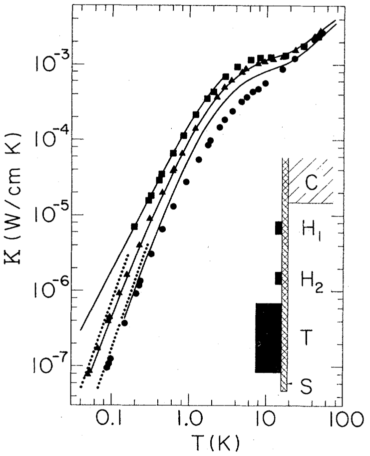

FIG. 1. Thermal conductivity of borosilicate glass. Circles: sample with 2.71×10^6 holes/cm^2, $d=5.4\times10^{-4}$ cm, $l_h=5.2\times10^{-4}$ cm; triangles: 1.57×10^5 holes/cm^2, $d=2.2\times10^{-3}$ cm, $l_h=2.2\times10^{-3}$ cm; squares: sample without holes. The curves are from calculations described in the text. The inset shows schematically the method of measurement. C—cold finger held at constant temperature during a measurement; S—sample, edge view; H—electrical heaters; T—resistance thermometer. The distance H_1-H_2 was typically 6×10^{-2} cm for low-temperature measurements. In the high-temperature regime this was increased to ≈ 0.5 cm.

is shown schematically in the inset of Fig. 1. For data below 2 K, the heaters were films of vapor-deposited Constantan and the thermometer was a chip from a Speer carbon resistor.[19] This thermometer was calibrated against a cerium-magnesium-nitrate magnetic thermometer which in turn was calibrated against the vapor pressure of ^{3}He. For data above 2 K, Manganin wire heaters and a calibrated germanium thermometer were used. To obtain a datum, power $\dot{Q}$ was first put into the heater H_1 and the temperature measured with thermometer T. The power was then removed from H_1 and the same power, $\dot{Q}$, was put into the heater H_2. The second reading of the thermometer provided a difference in temperature from which the thermal conductivity could be calculated. Because the samples were so thin, and in some cases the number of holes so large, the thermal conductance was extremely small. At the lowest temperatures, the power to the heaters was ≈ 10 erg/day. Thus the length of the sample was kept as short as possible, and this dictated the use of two heaters rather than the usual practice of two (much larger) thermometers.

The data for three of the borosilicate glass samples are shown in Fig. 1. Our data for the glass without holes are in good agreement with other measurements on borosilicate glasses.[20-23] The porous samples are reduced in conductivity from the nonporous or bulk sample, not just at the lowest temperature as one might at first expect for boundary scattering, but to temperatures as high as 30 K. We look first at the lowest-temperature data where κ is nearly proportional to T^3, similar to the boundary-scattering–limited conductivity of a crystal. We can test our understanding of these data by using the prediction of the Debye model, $\kappa = Cvl/3 = (2\pi^2k^4l/15\hbar^3v^2)T^3$. For l we substitute for each sample the known mean free path l_h due to the holes and, for v, the appropriate average of the measured[24] acoustic sound velocities, $\bar{v}=3.58\times10^5$ cm/sec. The results are shown for the two porous samples in Fig. 1 as dotted lines. It is seen that this calculation agrees very well with the low-temperature limit of the thermal conductivities. Thus the specific heat of the phonons deduced from the thermal-conductivity measurements is simply the specific heat one obtains from the Debye model using the acoustic sound velocity. This is in contrast to calorimetric measurements of the specific heat of amorphous solids which show a T^3 component as large as 3 times the Debye specific heat.[2,3] We conclude that this "extra" T^3 component in the measured specific heat, as well as the component linear in T, comes from localized modes which do not contribute to heat flow. This conclusion was also obtained by Pohl, Love, and Stephens in measurements on fine glass fibers.[25]

Data were obtained on the polycarbonate samples only below ≈ 1 K because of the extreme thinness of the sheets. Again the lowest-temperature data were in good agreement with the Debye prediction using measured acoustic velocities.[26] Also, as should be expected, samples which differed in both densities and diameters of holes, but which had the same l_h, had the same conductivity.

The thermal-conductivity data at higher temperatures in Fig. 1 can be partially understood by assuming that the internal bulk scattering is the sum of two processes. The first is the scattering by "two-state" systems which gives[11,12] $l(\omega)\propto\omega^{-1}\times\coth(\hbar\omega/2kT)$. The second process is less well understood, but it is probably related to the irregularity of the amorphous structure. Although there are various ways of describing this mechanism, one generally ends up with something similar to a Rayleigh $l\propto\omega^{-4}$ scattering.[2,9] At lower temperatures the first process is more important, but above a few kelvins the second process begins to dominate. Of course, the ω^{-4} dependence must fail at high frequencies or l will become smaller than interatomic distances—an unphysical possibility.[7] In Fig. 1, the solid lines represent a calculation of the form

$$\kappa = \tfrac{1}{3}\int_0^{\omega_D} d\omega\, C(\omega) v l(\omega)\,, \tag{1}$$

where

$$C(\omega) = 3\hbar^3\omega^4 e^{\hbar\omega/kT}/2\pi^2 v^3 k T^2 (e^{\hbar\omega/kT} - 1)^2\,, \tag{2}$$

and

$$l(\omega) = \{[(kA/\hbar\omega)\coth(\hbar\omega/2kT)]^{-1} + [B(k/\hbar\omega)^4]^{-1} + l_h^{-1}\}^{-1} \tag{3}$$

for $\omega < (k/\hbar)(B/l_{\min})^{1/4}$, and $l = l_{\min}$ for $\omega \geq (k/\hbar) \times (B/l_{\min})^{1/4}$. In the calculations, we have selected $A = 1.56\times 10^{-3}$ cm K to fit the data for the sample with no holes, $B = 0.51$ cm K^4 to fit the data for the sample with 22-μm holes, $l_{\min} = 5\times 10^{-8}$ cm, and $\hbar\omega_D/k = 275$ K. The results are rather insensitive to the last two parameters. A simple qualitative physical interpretation of the curves is that only phonons having a characteristic temperature ≈ 3 K contribute to κ in the region of the plateau, as though there were an effective Debye temperature of ≈ 10 K. Equivalently the curves[27] show how the plateau in κ comes from a rapid drop in phonon mean free path with increasing frequency. We note that a dominant-phonon approximation is not appropriate here for instead of a plateau we would have $\kappa(T) \propto C(T) l(T) \propto T^3 T^{-4} = T^{-1}$. The plateau should occur in the same temperature range for all amorphous materials since it occurs when the Rayleigh-type scattering becomes dominant, namely at $T_{\text{plateau}} \approx (B/A)^{1/3}$. Thus T_{plateau} is fairly insensitive to the magnitude of the constants A and B.

The curve, with no further adjustment of the parameters, calculated for the sample containing 5.4-μm holes does not agree with the data in the 1–10-K range. This may simply reflect a failure of "Matthiessen's rule" used in Eq. (3).[28] On the other hand, one could obtain a better fit for this sample (but a worse fit for the sample with 22-μm holes) by assuming that the density of two-state systems, as a function of energy ϵ, is increased by a factor of $1 + \beta(\epsilon/k)^2$. This would not only account for the "extra" T^3 contribution to the specific heat, but is required by Piché *et al.*[16] to fit their sound-velocity data in fused silica. The value of β determined from the sound velocity and ths specific heat agree. Because of the primitive state of the theoretical picture, however, we prefer not to perform further curve fitting.

We therefore do not have a quantitative understanding of the thermal conductivity of amorphous dielectrics. However two qualitative aspects find strong support in the present data. The first is that the thermal carriers are phonons having acoustic velocities. Thus the additional T^3 component observed in the specific heat[3] is related to nonpropagating modes. The second is that the thermal carriers at temperatures up to ≈ 30 K are low-frequency phonons having a characteristic temperature of $\lesssim 3$ K. This produces a plateau which is characteristic of the thermal conductivity of amorphous materials.

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*This research was supported in part by the National Science Foundation, Grants No. GH 33634 and No. GH 39135.

†National Science Foundation Fellow.

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Measurement of the Spatial Distribution of Electron-Hole Drops in Ge

M. Voos,* K. L. Shaklee, and J. M. Worlock
Bell Telephone Laboratories, Holmdel, New Jersey 07733

(Received 8 August 1974)

We have determined the radius and spatial distribution of electron-hole droplets in Ge at 2 K excited by a 100-mW focused beam of 5145-Å light. The droplet distribution can be approximated by a uniform hemispherical cloud of radius ≈1 mm containing droplets with radii of 2.0 ± 0.5 μm. These results disagree with solutions of simple diffusion equations and with recent reports of the observations of single large droplets with radii ≈1 mm.

Since the theoretical prediction of Keldysh[1] in 1968 of the existence of electron-hole drops, and the interpretation of luminescence data in Ge in terms of this model by Pokrovskii and Svistunova[2] in 1969, there has been a considerable amount of experimental and theoretical effort expended on the problem of the gas-liquid phase transition in a nonequilibrium electron-hole plasma. Most of the work to date has been devoted to measuring and understanding quantities such as the binding energy[3-7] and the liquid density.[3,5,7-10] Although some efforts have been made to study the spatial distribution of electron-hole droplets in Ge using microwave[11] and luminescence techniques,[3,12-14] these techniques are not able to give absolute measurements of the electron-hole density, and hence are not able to provide a complete picture of the electron-hole droplet (EHD) distribution.

Recently Worlock, Damen, Shaklee, and Gordon[15] (WDSG) have shown that it is possible to determine the EHD concentration and the total density of nonequilibrium electron-hole excitation in Ge by measuring the attenuation and the scattering of light at 3.39 μm.

In this paper we report the results of measurements made using the technique of WDSG to study germanium at ≈ 2 K, excited by a 100-mW focused beam of 5145-Å light. We have measured (a) the radius r_0 of electron-hole drops and their spatial distribution $\gamma(\vec{R})$, and (b) the spatial distribution $\rho(\vec{R})$ of the total nonequilibrium electron-hole excitation. We find that $\rho(\vec{R})$ can be approximated by a uniformly dense hard hemisphere of radius $R_0 = 1.05$ mm centered on the pump spot and containing an average electron-hole density $\approx 10^{15}$ cm^{-3}. From the light-scattering results we conclude that this hemisphere is a cloud of drops with radii $r_0 = 2.0 \pm 0.5$ μm and containing most of the nonequilibrium excitation. Such a spatial distribution is contrary to the predictions of simple diffusion theory[16] and is not understood