PHYSICAL REVIEW B VOLUME 12, NUMBER 10 15 NOVEMBER 1975

Boundary scattering of phonons in noncrystalline materials*

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(Received 28 April 1975)

Thermal-conductance measurements on thin Mylar and glass plates indicate that abrasion of the plate surfaces does not suppress specular reflection of phonons, contrary to the behavior in crystalline materials. This reinforces the suggestion that nonspecular reflection at crystal surfaces is caused primarily by lattice defects—defects which are absent in amorphous materials.

I. INTRODUCTION

As discussed in the previous paper[1] the thermal conductivities κ of noncrystalline materials are very similar in both magnitude and temperature dependence, independent of the constituents of the amorphous material. The data reported in the present paper represent our initial attempt to learn something about the excitations involved in the propagation of thermal energy in amorphous materials by measuring both κ and the boundary scattering or geometrical mean free path, l, in the kinetic expression

$$\kappa = \tfrac{1}{3} C v l . \tag{1}$$

In brief, we compared the κ of bulk samples (κ_∞) and of very thin sheets (κ). If acoustical phonons were the heat carriers, one would expect boundary scattering of phonons to reduce κ at temperatures below ≈ 1K.[2] Thus, the ratio κ_∞/κ would increase from unity at temperatures $T \gtrsim 1$K to much greater than unity at $T < 0.1$K as would happen in a crystalline material having $\kappa_\infty \propto T^2$. Instead the measured ratio κ_∞/κ remained close to unity at all temperatures, indicating either that phonons were not involved or, more likely, that the phonons were reflected specularly by the surfaces. Attempts to roughen or damage the surfaces to reduce specular reflection essentially did not change κ_∞/κ.

Analysis of these results had to wait until the work reported in Ref. 1 was completed. That is, until we knew that κ was provided by acoustic phonons we could not analyze our earlier data. It is concluded from the two materials used in the present measurements that, in contrast to the case of crystalline materials, it is difficult to suppress specular reflection of phonons from the surface of a noncrystalline sample by using mechanical abrasion techniques, at least at temperatures below ≈ 1 K. The results and a discussion of these results are presented in Sec. III.

A general treatment or review of the role of boundary scattering in phonon thermal transport does not appear in the literature, and occasionally incorrect or misleading formulas or statements have been presented in papers on thermal conducivity. In Sec. II, therefore, we summarize the theoretical and experimental situation for the more widely studied case of crystalline materials. This review will provide a background for the discussion of the phonon thermal conductivity of amorphous materials.

II. REVIEW OF BOUNDARY SCATTERING

A. Experiment

It has been well established empirically that for crystalline materials the lattice thermal conductivity κ is influenced by phonon scattering due to the presence of boundaries or surfaces, provided those surfaces have been abraded.[3] Without abrasion the thermal conductance of the sample may be much larger than expected in the boundary scattering limit. This larger conductance is assumed to be due to phonons reflecting specularly from the surface. This is a process which leaves the flow of heat unaltered.

Although boundary scattering has been used routinely in calculations for fitting low-temperature thermal-conductivity data, the mechanism of phonon scattering and the reason for the scattering being apparently independent of frequency are not understood. The mechanism first suggested was diffuse scattering of phonons caused by the roughness of the surface produced by abrasion.[3] But there is evidence that nonspecular reflections occur predominately in the damaged region immediately beneath the abraded surface and that, at least in some cases, the surfaces appear black in an optical sense.[4,5] That is, the phonons are thermalized so that upon leaving the surface they are independent of the incident phonons in energy (frequency) as well as in direction of propagation. Thus, the words "diffuse reflection" or "diffuse boundary scattering" may not accurately represent the scattering process and should be used advisedly.

Worlock[6] suggested that nonspecular reflection may be caused by the dense tangle of dislocations immediately below the abraded surface. Various abrasion, polishing, etching, and thermal treatments support the view that dislocations and/or other lattice defects are responsible.[4,5,7,8] Explicit evidence of the dynamic role of dislocations is obtained from γ-ray irradiation experiments[8] in which the resulting point defects apparently pin the dislocations, thus suppressing the localized excitations associated with dislocations.[9] There is also evidence that the *apparent* boundary at which the phonons scatter lies within the damaged region.[10] This would be of importance in the analysis of small samples, where the thickness of the damaged layer is significant relative to the smallest sample dimension.

At very low temperatures, some specular reflection may reappear at an abraded surface depending on the extent to which the surface has been damaged.[9,11] This indicates that the scattering mechanism is to some extent wavelength dependent. In the case of Ge it has been reported[12] that even above 1 K dislocations (or other lattice defects) fail to eliminate specular reflections. Independent measurements on Ge,[13] however, indicate a strong influence from surface damage in agreement with other crystalline materials.

Occasionally boundary scattering appears to dominate κ, but the phonon mean free path l deduced from κ is not that expected from the simple expression $\kappa = \frac{1}{3}Cvl$, with l related to a characteristic dimension of the sample. This may happen if one or more phonon modes are strongly scattered within the bulk of the crystal so that only the remaining modes reach the boundaries,[9] or if the bulk scattering has a very strong frequency dependence such that only phonons within a certain frequency spectrum can reach the boundaries.[1,14] The same effect will appear in anisotropic crystals if phonon focusing is ignored,[15] and one should be aware of this problem in data analyses appearing prior to approximately 1970.

In summary, there is considerable experimental evidence that phonons are scattered nonspecularly at crystalline surfaces containing dislocations or other lattice defects produced by some technique of abrasion. At least in some cases the phonons are thermalized at these boundaries.

B. Theory

The original calculation[16] by Casimir for the boundary-scattering-limited phonon thermal conductivity assumes that all phonons arriving at the boundary are absorbed and reradiated with a frequency distribution determined by the temperaature of the boundary. If certain simplifying assumptions are made, such as no internal scattering and no anisotropy, one finds for an infinitely long cylinder an average phonon mean free path l equal to d, the diameter of the cylinder. That is, $\kappa = \frac{1}{3}Cvl = \frac{1}{3}Cvd$, where c is the specific heat of the phonons and v is an appropriate average of the sound velocities. There is some confusion in the literature over what happens for rectangular geometries, so we have attempted to clarify the situation in the Appendix. In particular, we will be interested in the case where the thickness is much smaller than the width and length of the sample.

When internal or bulk phonon scattering is included, the problem becomes more complicated. In the case of boundary scattering of electrons expressions have been worked out for a thin plate[17] and a cylindrical rod.[18] But these formulas apply as well to phonon boundary scattering as shown by Baush and Waidelich.[19] If l_i is the phonon mean path in the bulk,

$$l = l_i \left(1 - \frac{3l_i}{2t}(1-p) \int_1^\infty (x^{-3} - x^{-5})(1 - e^{-tx/l_i}) \times (1 - p\, e^{-tx/l_i})^{-1}\, dx \right) \quad (2)$$

for a thin plate of thickness t with a fraction p of the phonons colliding with the boundary being speculary reflected.[20] In the case of a cylindrical rod, a similarly complicated formula may be approximated[20] to within a few percent by the phonon equivalent of Mathiessen's rule, $l = (d^{-1} + l_i^{-1})^{-1}$. It is here being assumed, of course, that all phonon modes have a similar l_i.

Baush and Waidelich[19] have attempted to show theoretically that dislocations may be responsible for the nonspecular reflection at a damaged surface. They use a shorter phonon relaxation time in the damaged layer than in the bulk of the crystal. Unfortunately, although dislocations do appear to be involved from empirical evidence, the appropriate relaxation time is not known.[9] Hence in the present paper we will continue to assume that all phonons relax thermally at the boundary except a fraction p which are specularly reflected. Also, since the measurements are made at low temperature, it will be assumed that phonon normal processes are not important.[21]

III. RESULTS AND DISCUSSION

The samples were made from a 2.9×10^{-4}-cm-thick Mylar sheet or from 7.1×10^{-3}-cm-thick (Corning 0211) glass plates. Thicker Mylar sheets were measured but provided no additional information, and so will not be discussed. The techniques used in the measurements have been presented in Ref. 1, and will not be repeated here.

The thermal conductivities of the as-recieved materials are presented in Fig. 1. The thermal conductivity of the Mylar sheet agrees to $\approx 20\%$ with the measurements on thicker sheets, and is in reasonable agreement with a previous measure-

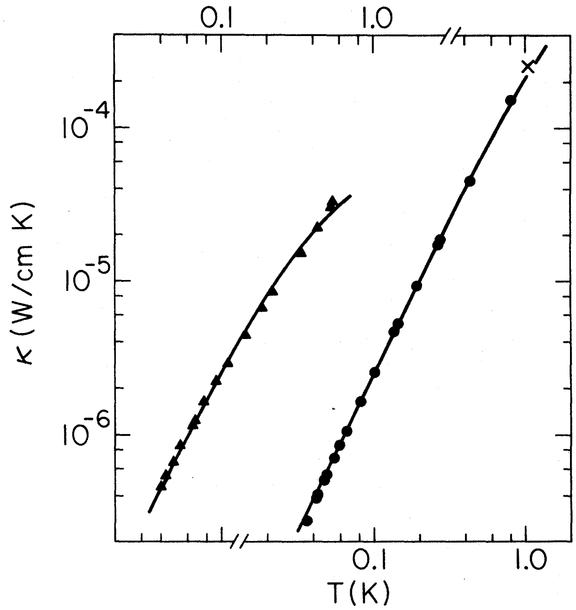

FIG. 1. Thermal conductivity of a 2.9×10^{-4}-cm-thick Mylar film (▲) and two 7.1×10^{-3}-cm-thick glass plates (●,×). Other (×) data lie directly under the data shown. Mylar data refer to the top temperature scale, the glass to the bottom scale. Curves through the data were computed as explained in the text.

ment made using an entirely different technique and geometry.[22] Other measurements on the glass are not available; however, the thermal conductivity of this glass is within 20% of that of the borosilicate glass used in Ref. 1. In brief, the presence of the surfaces has not altered significantly the thermal conductivity of the present samples. Since phonons are known to transport the thermal

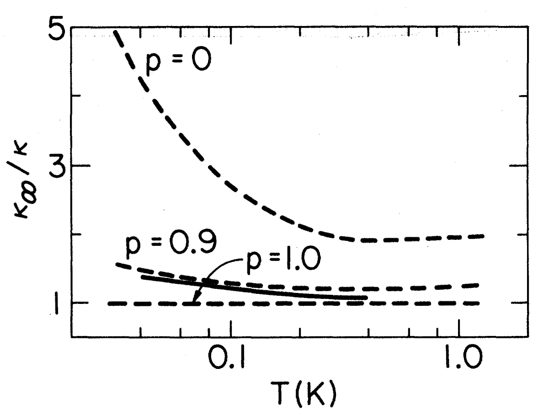

FIG. 2. Ratio, for Mylar, of the thermal conductivity κ_∞ of a film with smooth surfaces (i.e., κ of the bulk material) to that of the abraded sample. Solid curve is the experimental result for a sandblasted sample. Dashed curves are the results of theoretical calculations for different fractions p of specularly reflected phonons.

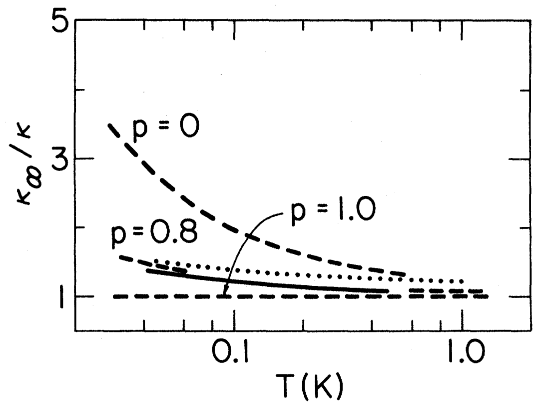

FIG. 3. Ratio, for glass, of the thermal conductivity of a plate with smooth surfaces (i.e., κ bulk material) to that of abraded samples. Dashed curves are the results of theoretical calculations for different fractions p of specularly reflected phonons. Solid curve is the experimental result for mechanically ground surfaces; dotted curve is for a sandblasted sample. Latter curve is probably systematically ≈10% high as explained in the text.

energy,[1] the majority of the phonons must have been reflected specularly from the surfaces. It will be shown below that, were this not the case, the thermal conductivity would have been smaller by ≈400% at the lowest temperatures.

Specular reflection of phonons from the smooth surfaces of these samples is not unreasonable in light of the discussion in Sec. IIA. We therefore attempted to damage the surfaces in the manner used for crystalline materials. The surfaces were etched, were mechanically ground with 27-μm abrasive particles, or were sandblasted with the same abrasive in an air-borne jet. There was very little change in the thermal conductivity of the samples, indicating that specular reflection was still dominant.

The above results are presented more quantitatively in Figs. 2 and 3 as κ_∞/κ, the ratio of the thermal conductivity of the bulk material (thickness $t\to\infty$) to that of the film or plate. Actually the data of the as-received samples with smooth surfaces are used as a good approximation for κ_∞, and so Figs. 2 and 3 show the change in κ resulting from surface damge. Since data points were not obtained at the same temperatures for the various samples, curves were smoothed through the individual sets of data and the ratios of these curves as a function of temperature are plotted in Figs. 2 and 3. The use of the ratio κ_∞/κ also reduces the importance of systematic errors introduced in determining the geometry of the samples. This is especially true for the Mylar since the heaters were placed very close together making the "length" of the specimen difficult to estimate.[1] The *same* spacing, however, was used for all samples.

Figure 2 gives the ratio κ_∞/κ for Mylar film with sandblasted surfaces. Mechanically ground surfaces had the same appearance as the sandblasted surfaces when viewed in a scanning electron microscope, and so were not measured. The surfaces appeared rough with a typical asperity of $\approx 10^{-4}$ cm. Were phonons actually to impinge on the visible surface, diffuse scattering should have occurred down to ≈ 0.01 K. The ratio κ_∞/κ expected theoretically under this condition can be obtained from[23]

$$\kappa(T) = \frac{1}{3}\int_0^\infty C(\omega) v l(\omega)\, d\omega \ , \tag{3}$$

where, from the Debye model,

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

and $\ell(\omega)$, the net phonon mean free path, is obtained from Eq. (2). For the internal or bulk mean free path ℓ_i to be inserted in Eq. (2) we use, for *convenience*, that discussed in Ref. 1 (the nonresonant term is negligible at low T),

$$l_i(\omega, T) = \{ [(kA/\hbar\omega)\coth(\hbar\omega/2kT)]^{-1} + [B(k/\hbar\omega)^4]^{-1} \}^{-1} . \tag{5}$$

Parameters A and B are selected to give a reasonable fit to the measured bulk thermal conductivities κ_∞ of the samples which, as noted above, are closely approximated by the data of Fig. 1. The curves of Fig. 1 were in fact obtained using, for Mylar,[24] $A = 2.2\times10^{-4}$ cm K and $B = 2\times10^{-4}$ cm K^4 and, for the glass,[25] $A = 2.6\times10^{-3}$ cm K and $B = 0.5$ cm K^4. Equation (5) need not reproduce κ_∞ precisely since only the theoretical ratio κ_∞/κ is of interest. The adjustable parameter is the fraction p of phonons reflected specularly from the surfaces. Calculated ratios of κ_∞/κ are shown in Fig. 2 as dashed lines for three values of p. With $p=0$ (no specular reflection) theoretical reduction in κ near 0.04 K would be $\approx$400%. The data indicate that over 90% of the phonons undergo specular reflection from the severely abraded surfaces.

Similar information for the glass is presented in Fig. 3. The solid curve is for a mechanically ground surface. A chemically etched surface, followed by mechanical grinding, gave the same ratio. The ground surfaces appeared extremely rough when viewed under a scanning electron microscope, with an asperity of $\approx 10^{-3}$ cm. Had the phonons reached the visible surface, diffuse scattering should have occurred at all temperatures of the measurement. Instead over 80% of the phonons were reflected specularly. It may be that the specular reflection occurred at cracks near the bases of the tall, narrow peaks formed by abrasion. Such cracks were occasionally observed in sectioned samples using a scanning electron microscope.

The dotted curve in Fig. 3 is for a sandblasted sample. The surfaces were pocked or pitted. The width of the rounded pits was $\approx 7\times10^{-4}$ cm, with a depth of about one-half this value. In such a case primarily specular reflection would be expected, and indeed the data of Fig. 3 are nearly horizontal with a mean value of $\kappa_\infty/\kappa \approx 1.2$. It is likely that the actual ratio is closer to 1.1. This is because the thickness t used to compute κ from the thermal conductance was in all cases measured mechanically. In this sandblasted sample the mean reflecting boundary is certainly closer to the bottom of the pits, which would reduce the effective t by $\approx$10%. A similar but less definitive statement can be made about the other samples of Figs. 2 and 3. In brief, the experimental ratios of κ_∞/κ are maximum values, and might be systematically a few percent *smaller* corresponding to an even greater amount of specular reflection.

Other chemical etching techniques on the glass plates did not provide sufficiently rough surfaces to cause diffuse reflection, and thus κ was not measured for those samples. Stephens experienced similar difficulties.[26] He measured the thermal conductivities of the fine soda-silica glass fibers and interpreted the results as indicating specular reflection of phonons from the surfaces. The specular reflection *could be suppressed* however, with varying success, by chemically etching the surfaces. Presumably this provided a sufficiently rough surface to produce diffuse phonon scattering. This technique is sensitive to etchant and to the type of glass used. For example, the etchant used by Stephens did not appropriately roughen our glass plates.

The results available thus far may be summarized as follows. (i) In crystalline materials nonspecular boundary scattering of phonons is thought to occur in the thin damaged layer beneath an abraded surface. In noncrystalline materials it has not been possible to produce this effect. This implies that defects indeed are responsible for the nonspecular reflections in crystals and, not surprisingly, that amorphous materials do not support the kind of defects common to crystals. Therefore (ii) nonspecular boundary scattering in amorphous materials must be provided by diffusive scattering from a truly topographically rough surface.

APPENDIX

According to Casimir,[16] for an isotropic, infinitely long rod of uniform cross section with a constant temperature gradient ∇T in the x direction, the heat flow $\dot{Q}$ is

$$\dot{Q} = \frac{\pi k^4 T^3 \nabla T}{10\hbar^3 v^2}\iint\iint (x_{12}\cos\theta_1\cos\theta_2/r_{12}^2)\, dS_1\, dS_2\, , \tag{A1}$$

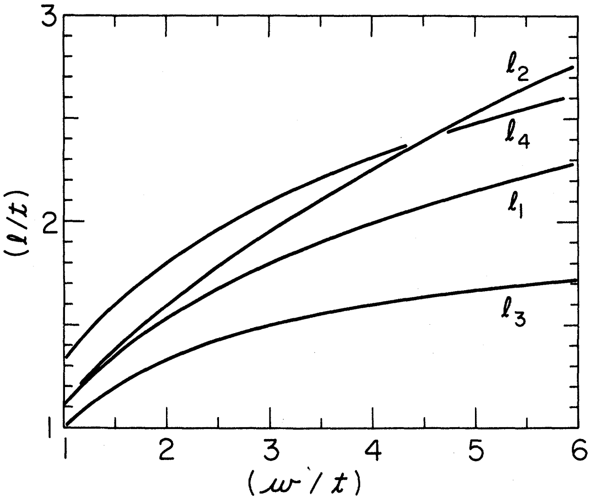

FIG. 4. Ratio of l/t, the net phonon mean free path in a long rectangular rod divided by the thickness of the rod, vs the ratio w/t, the width divided by the thickness, for the case of no specular reflection from the surfaces and no internal or bulk scattering mechanism. Exact calculation is represented by curve l_1. Other curves are discussed in the Appendix.

where dS_1 is an element of area on the boundary of the rod, dS_2 is an element of area in the cross section of the rod at $x=0$, r_{12} is a vector connecting dS_1 to dS_2, x_{12} is the x component of r_{12}, θ_1 and θ_2 are the angles between r_{12} and the normals to dS_1 and dS_2, and k and the other symbols have their usual meanings.[23] Defining a mean free path l_b for boundary scattering through the formulas $\kappa = \frac{1}{3}Cv\,l_b$ and $C = 2\pi^2k^4T^3/5v^3\hbar^3$, and noting $\kappa = (\dot{Q}/A)/\nabla T$, where $A = \iint dS_2$ is the cross sectional area, one obtains

$$l_b = \frac{3}{4\pi}\,\frac{\iiiint (x_{12}\cos\theta_1\cos\theta_2/r_{12}^2)\,dS_1\,dS_2}{\iint dS_2}. \quad \text{(A2)}$$

Corrections to Eq. (A2) for a rod of finite length are discussed in Ref. 15. If the rod has a rectangular cross section with thickness t and width w, then

$$l_b = \frac{3}{2\pi w t}\int_0^t dy_1\int_0^t dy_2\int_0^w dz_2\int_{-\infty}^{+\infty} dx_1 \times \frac{x_1^2\,z_2}{[x_1^2+z_2^2+(y_1-y_2)^2]^2} + \int_0^t dy_2\int_0^w dz_1\int_0^w \times dz_2\int_{-\infty}^{+\infty} dx_1\,\frac{x_1^2\,y_2}{[x_1^2+(z_1-z_2)^2+y_2^2]^2}\,, \quad \text{(A3)}$$

$$l_b = \tfrac{1}{4}t\{[1-(1+n^2)^{3/2}+n^3]n^{-1} + 3n\ln[n^{-1} + (1+n^{-2})^{1/2}] + 3\ln[n+(1+n^2)^{1/2}]\}, \quad \text{(A4)}$$

where $n = w/t$, as has been obtained previously.[10,15]

This, however, is not the formula typically used to fit thermal conductivity data. Instead, reference is made to a "Casimir length" l_c which is assumed to be the phonon mean free path due to boundary scattering. Since different authors use different expressions for l_c, we compare these different expressions to each other and to Eq. (A4) in Fig. 4. That calculated from Eq. (A4) is labeled l_1. Also $l_2 = (4A/\pi)^{1/2}$, where A again is the cross-sectional area of the rod,[27,28] $l_3 = 4A/P$, where P is the perimeter of the rod,[14,29] and[30]

$$l_4 = (3t/4)\{\ln[n+(1+n^2)^{1/2}] + n\ln[n^{-1}+(1+n^2)^{1/2}]\}.$$

Other forms[31] of $l_c \alpha A^2$ may be scaled from the plot for l_2. In each case $p=0$, i.e., there is no specular reflection. It is seen from Fig. 4 that l_2 gives the best approximation to the exact expression l_1 as the cross section approaches a square. It also has the advantage of giving the correct mean free path for a circular cylinder.

One must be careful in using these expressions as $n = w/t$ becomes large and the rod becomes a thin plate or film. In the limit of large n

$$l_1 \to (3t/4)\ln(3.3\,w/t), \quad \text{(A5)}$$

and it would appear that the mean free path and hence the conductivity becomes infinite. This comes from phonons traveling almost parallel to the plane of the film. In reality, the thermal conductance is then governed by the intrinsic mean free path l_i in the bulk. If one uses Eq. (2) for a thin plate in the limit of $l_i \gg t$, then[20] $l \to (3t/4)\ln(1.5 l_i/t)$. This is very similar to Eq. (A5) with width w replaced by $\approx \frac{1}{2}l_i$. In other words, a thin film acts like a rectangular rod with an equivalent "width" determined by the bulk or internal phonon scattering.

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*Research supported in part by the National Science Foundation under Grants Nos. DMR-7203026 and GH-39135.

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[25]We have used $v=4.0\times10^5$ cm/sec estimated from data on elastic moduli at room temperature provided by the Corning Glass Works. This glass is $\approx 63\%$ SiO_2, 8% B_2O_3, 7% K_2O, 7% Na_2O, and 5% TiO_2; see S. S. Kistler, J. Am. Ceram. Soc. 45, 59 (1962).

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