

## Thermal Conductivity of Silicon in the Boundary Scattering Regime\*

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Thermal-conductivity measurements were made on high-purity silicon samples with both rough-lapped and polished surfaces in the temperature range 1–4°K where boundary scattering of the phonons is dominant. Rough-surfaced rods cut in the [111] and [110] directions gave results in good agreement with the theory for completely diffuse surface scattering, but in the [100] direction there appears to be an appreciable fraction of specular reflection. The latter depends only on the heat-flux direction, not the surface orientations. With polishing, the specularity increases, and can be brought to over 90% at the lowest temperatures. The size-effect variation of the conductivity under such conditions is in excellent agreement with the theory. The thermal conductivity appears to be a sensitive tool for detection of surface damage.

### I. INTRODUCTION

IN very pure and perfect single crystals of dielectric materials at low temperatures, phonon scattering occurs mostly at the crystal surface, and the thermal conductivity does not have a unique value for the material but depends upon the crystal dimensions. This “size effect” of the thermal conductivity was first observed experimentally by de Haas and Biermasz<sup>1</sup> and an approximate theoretical explanation was developed by Casimir.<sup>2</sup> The collisions with the surface were assumed to result in diffuse scattering, in which the phonons are considered to be absorbed by the surface and then reemitted with an energy distribution dependent upon the local temperature. Under these conditions the energy flux originating at a surface area element  $d\sigma_1$  and penetrating an area  $d\sigma_2$  in a planar cross section of the rod is

$$d^4F = \frac{(\pi kT)^4 \cos\theta_1 \cos\theta_2}{15h^3 r^2} \sum_{i=1}^3 [v_i(\hat{r})]^{-2} d\sigma_1 d\sigma_2, \quad (1)$$

where  $r$  is the distance from  $d\sigma_1$  to  $d\sigma_2$ ,  $\hat{r}$  is a unit vector in this direction,  $\theta_1$  and  $\theta_2$  are the angles between  $\hat{r}$  and the normals to  $d\sigma_1$  and  $d\sigma_2$ , respectively, and  $v_i(\hat{r})$  is the velocity of the  $i$ th acoustic mode in the direction of  $\hat{r}$ . If we assume that a linear temperature gradient exists along the crystal, then

$$T^4(z) \cong T^4(0) + 4T^3(dT/dz)z, \quad (2)$$

and the energy flux through the entire cross section is

$$F = 4T^3 \frac{\pi^4 k^4}{15h^3} \frac{dT}{dz} \iiint \frac{\cos\theta_1 \cos\theta_2 d\sigma_1 d\sigma_2}{r^2} \times \sum_{i=1}^3 [v_i(\hat{r})]^{-2}. \quad (3)$$

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<sup>1</sup> W. J. de Haas, and T. Biermasz, *Physica* **2**, 673 (1935); **4**, 754 (1937); **5**, 47 (1938).

<sup>2</sup> H. B. G. Casimir, *Physica* **5**, 495 (1938).

Casimir considered only isotropic crystals, in which the phonon velocities  $v_i(\hat{r})$  are independent of direction. The integration is then simplified as the factor  $v_i^{-2}$  is a constant, and for a cylindrical crystal of radius  $R$  and infinite length, the thermal conductivity, defined as  $F/\pi R^2(dT/dz)$ , is given by

$$\kappa_{\text{iso}} = 4T^3 \frac{\pi^4 k^4}{15h^3} \sum_{i=1}^3 \frac{4\pi}{3} v_i^{-2} (2R). \quad (4)$$

Now, the specific heat at low temperatures is<sup>2</sup>

$$C_{\text{iso}} = 4T^3 \frac{\pi^4 k^4}{15h^3} 4\pi \sum_{i=1}^3 v_i^{-3}. \quad (5)$$

Thus, by defining an average phonon velocity as

$$\langle v \rangle = \frac{\sum_{i=1}^3 v_i^{-2}}{\sum_{i=1}^3 v_i^{-3}}, \quad (6)$$

the thermal conductivity can be expressed in the form familiar in gas kinetic theory:

$$\kappa_{\text{iso}} = \frac{1}{3} C_{\text{iso}} \langle v \rangle l, \quad (7)$$

with

$$l = l_c \equiv 2R, \quad (7')$$

where  $l$  is the phonon mean free path and Eq. (7) is its definition.  $l_c$  is termed the Casimir length, and indicates the special value of  $l$  for an infinitely long crystal with perfectly diffuse walls.

The theory of Casimir was extended by Berman, Simon, and Ziman (hereafter referred to as BSZ)<sup>3</sup> in two respects. They took into account that some of the phonons striking the crystal surface might reflect specularly, increasing the phonon free path and thus the conductivity, and that phonons could also originate at and be reflected from the ends of a finite length crystal. These considerations yield a modified size effect, in which the conductivity is no longer simply proportional to the crystal diameter, but is dependent upon the ratio of crystal radius to length, and upon,

<sup>3</sup> R. Berman, F. E. Simon, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A220**, 171 (1953).

of course, the surface "roughness factor"  $f$ . The latter is taken to be a measure of the diffuseness of scattering and varies between  $f=1$  for perfectly diffuse scattering and  $f=0$  for perfectly specular reflection. This model continues to predict a  $T^3$  dependence, but the magnitude of the conductivity at any temperature may vary widely as  $f$  departs from 1 and  $R/L$  departs from zero.

BSZ<sup>3</sup> also presented an experimental test of their theory. The measurements were on diamond with ground surfaces, and the conductivity showed a  $T^{2.8}$  dependence and agreed reasonably well with the curve for  $f=0.60$ . A later study by Berman, Foster, and Ziman<sup>4</sup> on single crystals of sapphire revealed a  $T^3$  dependence for the conductivity, and agreement of the magnitude within 10% of that given by the BSZ theory for  $f=1$ . Measurements were also made on sapphire crystals with flame-polished surfaces. These surfaces gave some specular reflection,  $f$  being 0.70 at 6°K. In addition, the temperature dependence of the conductivity with flame-polished surfaces was  $T^{2.7}$ , indicating an increase in the fraction of specular reflection with increasing phonon wavelength.

Since then, a variety of measurements have been made on dielectric materials over a wide temperature range that includes the boundary scattering regime. The most recent measurements on silicon are those of Glassbrenner and Slack.<sup>5</sup> They find "agreement with theory" in the boundary scattering regime, although a discussion of the degree of agreement is not given. Holland<sup>6</sup> reports agreement within 10% in the boundary scattering if the length-to-width ratio correction is applied in several elemental and compound semiconductors. Particular attention was given to the boundary scattering in the work of Seward<sup>7</sup> on KCl, LiF, and KBr, and Thacher<sup>8</sup> on LiF.

The present study was begun with the following purposes in mind: First, at the time the work was started, the thermal conductivity in the boundary scattering regime had not been fully investigated with crystals of high purity and perfection, as are now available. A careful investigation of the size-effect for the crystals with rough surfaces was planned, so that comparison with existing theory could be made. Second, once the behavior of the thermal conductivity for rough surfaces was well understood, an investigation of crystals with very smooth surfaces was planned. It was contemplated that the scattering of phonons might sensitively reflect the nature and degree of imperfections present in the crystal surface. Those imperfections that would scatter phonons most strongly would be of a size comparable to the dominant phonon wavelength, which

is of the order of 100 Å in the liquid-helium range, and would thus be difficult to investigate by other methods. Silicon was chosen as a material since good quality single crystals of high purity are readily available, and because a variety of methods for producing highly polished surfaces are known. All of our measurements have been confined to the temperature range 1.3–4.2°K, where boundary scattering is dominant.

## II. EXPERIMENTAL METHODS

The apparatus for the steady-state measurement of the thermal conductivity is of fairly standard design. The thermometers are of the germanium resistance type manufactured by Texas Instruments, Inc.<sup>9</sup> They have a resistance of 2000 Ω at 4.2°K and 2.5 MΩ at 1.3°K, giving a very high sensitivity. Thermal contact to the germanium element is made through one of the 10-mil platinum leads. The thermometers were calibrated against the helium vapor pressure using the 1958 He<sup>4</sup> scale.<sup>10</sup> It is estimated that over most of the range 1.3–4.2°K, the calibration is accurate to better than ±3 mdeg. A sensitive manostat of a design similar to that of Walker<sup>11</sup> was used for temperature stabilization.

The thermometer resistances were measured on an ac bridge using a highly tuned amplifier of a design similar to that of Seward,<sup>7</sup> so that the power dissipated in the thermometers ranged from 10<sup>-8</sup> W at 4.2°K to 10<sup>-11</sup> W at 1.3°K. The warming of the thermometers by the dissipated power was small above 3°K, but became appreciable at lower temperatures. Consequently, to avoid introducing systematic errors in the temperature measurement, all thermometer resistances were determined with the bridge operating at its lowest power level, so that at any given temperature the thermometer resistance was determined each time at the same power level. The sensitivity of the bridge was such that it would then detect changes of a few parts in 10<sup>4</sup> in resistance, which corresponded to better than one part in 10<sup>4</sup> in temperature.

In order to be able to analyze the raw data on a computer, it was desirable to have an equation relating thermometer resistance to temperature. The best fit we could devise was of the form

$$T = T'(R) + T_e, \quad (8a)$$

with

$$\log_{10} T' = A - BX + C \tanh D(X - X_0), \quad (8b)$$

$$X = \log_{10} R.$$

The residual correction term  $T_e$ , which could amount to as much as 10 mdeg, was tabulated as function of  $T'$  at 0.1 deg intervals and computations were made by linear interpolation of the latter.

<sup>9</sup> Texas Instruments, Inc., 3609 Buffalo Speedway, Houston, Tex.

<sup>10</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Stds. **64A**, 1 (1960).

<sup>11</sup> E. J. Walker, Rev. Sci. Instr. **30**, 834 (1959).

<sup>4</sup> R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A231**, 130 (1955).

<sup>5</sup> C. J. Glassbrenner, and G. A. Slack, Phys. Rev. **134**, A1058 (1964).

<sup>6</sup> M. G. Holland, Phys. Rev. **134**, A471 (1964).

<sup>7</sup> W. D. Seward, Ph.D. thesis, Cornell University, 1965 (unpublished).

<sup>8</sup> P. D. Thacher, Phys. Rev. **156**, 975 (1967).

Thermal contact of thermometers to the sample is made with indium-faced copper clamps, lightly coated with Apiezon vacuum grease. Measurements of thermal contact resistances of this type showed that the thermometers were within 0.05 mdeg of the crystal temperature at their point of attachment. Similar clamps were used to introduce and remove the heat at the ends of the crystal. Adequate thermal isolation of the thermometers from the surroundings was assured by using as electrical leads coiled 20-cm lengths of 3-mil constantan wire tinned with solder so as to be superconducting, and by evacuating the experimental chamber to about  $10^{-6}$  Torr.

The thermal-conductivity measurements were made using the "two-heater method."<sup>12</sup> The thermal conductivity  $\kappa(\tau)$  for a rod of cross-sectional area  $A$  is determined from the relation

$$H = \kappa(\tau)A\Delta T/\Delta X, \quad (9)$$

where  $\Delta T = T_1 - T_2$  is the temperature difference between thermometers a distance  $\Delta X$  apart in the presence of the heat flux  $H$  along the rod, and  $\tau = \frac{1}{2}(T_1 + T_2)$  is the mean temperature. For  $\kappa$  proportional to  $T^3$ , the relative error in Eq. (9) is  $(\Delta T/2\tau)^2$  and is therefore negligible for  $\Delta T \lesssim 100$  mdeg. For thermometers of the above sensitivity,  $\Delta T$  can be determined to 2% accuracy using the two-heater method if  $\Delta T \lesssim 0.01T$ , so that a temperature difference between thermometers of some tens of mdeg is adequate. With the geometrical factors known to 3% accuracy, the measurements then have an over-all accuracy of 5%.

In addition to mounting the sample with clamps, some conductivity measurements were made with the heat introduced and removed from the crystal through soldered contacts to the ends of the crystal rod, and with the thermometers soldered to the sides of the crystal. The conductivities obtained in this manner were the same as with the clamped mounting, showing that the placement of the thermal contacts on the faces of the crystal rather than the ends did not introduce any significant anomalies in the temperature distribution. In all cases, the thermometer clamps were kept at least two diameters away from the end clamps. Typically, the thermometers were separated by a distance of 2 to 3 cm.

Thermal-conductivity measurements were made on samples cut from three different crystals, each from a different manufacturer. Crystal A, manufactured by Knaptic Electro-Physics,<sup>13</sup> was grown in the [111] direction. It is  $p$  type, with a room-temperature resistivity of 195  $\Omega$  cm, and an average dislocation density of 750 pits/cm<sup>2</sup>. Crystal B was obtained from Future-

craft Corp.,<sup>14</sup> and was grown in the [100] direction. It is  $n$  type, with a room-temperature resistivity of 500  $\Omega$  cm. Crystal C was obtained from Semi-elements, Inc.,<sup>15</sup> and was also grown in the [100] direction. It is  $n$  type, with a room-temperature resistivity of 3000  $\Omega$  cm. Although the method of growth of these crystals is not known with certainty, they all had the generally uniform cylindrical appearance characteristic of floating zone growth. Infrared-transmission measurements indicated that the absorption coefficient at the 9- $\mu$  absorption peak was about 1 cm<sup>-1</sup> for all three crystals. Since this absorption is comparable with the "background" normally observed,<sup>16</sup> we concluded that these crystals are free of the large concentrations of oxygen that have been observed<sup>17</sup> to cause a decrease in the thermal conductivity.

Typical samples had widths from 0.5 to 2 mm and were 30 to 40 mm in length. Samples cut from crystal A with the rod axis in the [111] direction exposed two {110} and two {11 $\bar{2}$ } rod faces. Sample numbers from this crystal are prefaced A1. Samples from crystals B and C with rod axes in the [100] direction were cut with two rod-face orientations. Those cut so that all exposed faces are {100} have sample numbers prefaced B2-2 and C2-2, respectively, while those cut so that all exposed faces are {110} have sample numbers prefaced B2-3 and C2-3. Samples were also cut from crystal C with rod directions [111] and [110], and are designated C1 and C3, respectively. Samples of type C3 had pairs of {100} and {110} faces.

### III. ANALYSIS OF DATA

The theory of Casimir, and its extension by BSZ, applies for isotropic crystals. For crystals which are anisotropic, such as silicon, the phonon velocities appear in an integral over all angles as indicated in Eq. (3), and this cannot readily be evaluated since no simple expressions for the velocities as functions of direction exist. The angular factor in Eq. (3) suggests that the largest contribution to the heat flux is made by phonons traveling in directions roughly 45° from the crystal axis. However, to simplify the analysis, let us instead consider the phonons traveling parallel to the rod axis. We then approximate Eq. (3) for a sample with a rod axis in the  $\hat{n}$  direction as

$$F(\hat{n}) = 4T^3 \frac{\pi^4 k^4}{15h^3} \frac{dT}{dz} \sum_{i=1}^3 [v_i(\hat{n})]^{-2} \times \int \int \int \int \frac{\cos\theta_1 \cos\theta_2}{r^2} z d\sigma_1 d\sigma_2, \quad (10)$$

<sup>14</sup> Futurecraft Corp., 1705 N. Chico Ave., South El Monte, Calif.

<sup>15</sup> Semi-elements, Inc., Saxonburg Blvd., Saxonburg, Pa.

<sup>16</sup> W. Kaiser and P. H. Keck, J. Appl. Phys. **28**, 882 (1957).

<sup>17</sup> M. G. Holland in *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961), p. 280.

<sup>12</sup> R. Berman, in *Experimental Cryophysics*, edited by F. E. Hoare, L. C. Jackson, and N. Kurti (Butterworths Scientific Publications, Ltd., London, 1961), p. 333.

<sup>13</sup> Knaptic Electro-Physics, 940 Industrial Ave., Palo Alto, Calif.

where the sum is over the acoustic phonon velocities for the  $\hat{n}$  direction. The conductivity is then given by

$$\kappa(\hat{n}) = 4T^3 \frac{\pi^4 k^4}{15h^3} \sum_{i=1}^3 [v_i(\hat{n})]^{-2} \frac{4\pi}{3} (2R). \quad (11)$$

This can clearly be put in the "kinetic theory" form of Eq. (7) by a suitable definition of  $\langle v \rangle$ . One approach is to note that the specific heat of the anisotropic crystal may be written

$$C = 4T^3 \frac{\pi^4 k^4}{15h^3} 4\pi \sum_{i=1}^3 \langle v_i^{-3} \rangle, \quad (12)$$

where the sum is over the *direction-averaged* velocities and is the same for all rod directions. The desired result is then obtained if we define the average phonon velocity as

$$\langle v(\hat{n}) \rangle = \sum_{i=1}^3 [v_i(\hat{n})]^{-2} / \sum_{i=1}^3 \langle v_i^{-3} \rangle. \quad (13)$$

Another approach, admittedly somewhat arbitrary, is to take

$$\langle v(\hat{n}) \rangle = \sum_{i=1}^3 [v_i(\hat{n})]^{-2} / \sum_{i=1}^3 [v_i(\hat{n})]^{-3}. \quad (14)$$

This, in effect, takes the specific heat to be that of phonons traveling in the  $\hat{n}$  direction.

The phonon velocities were determined from the elastic constants at  $-200^\circ\text{C}$ , given by McSkimin.<sup>18</sup> The room-temperature value  $2.332 \text{ g/cm}^3$  of the density of silicon was used, as the change in the density due to thermal contraction is small.<sup>19</sup> Results for the three principal directions are given in Table I.

The specific heat was taken from the values measured by Flubacher, Leadbetter, and Morrison.<sup>20</sup> All of our measurements on silicon were done in temperature range  $1.3\text{--}4.2^\circ\text{K}$ , so that the second term in the expression

$$C_v = aT^3 + bT^5 \quad (15)$$

may be neglected. The value of  $a$  is  $6.02 \text{ erg/cm}^3 \text{ deg}^4$ , and the corresponding characteristic temperature ( $\Theta$ )

TABLE I. Sound velocities in silicon at low temperatures ( $10^5 \text{ cm/sec}$ ).<sup>a</sup>

	[100]	[111]	[110]
$v_l$	8.47	9.42	9.18
$v_{l1}$	5.86	5.11	5.86
$v_{l2}$	5.86	5.11	4.68
$\langle v \rangle_1$	5.00	6.11	6.00
$\langle v \rangle_2$	6.22	5.42	5.41

<sup>a</sup>  $v_l$ ,  $v_{l1}$ , and  $v_{l2}$  are the velocities of the longitudinal and the two transverse acoustic modes, respectively;  $\langle v \rangle_1$  and  $\langle v \rangle_2$  are the averages as given by Eqs. (13) and (14), respectively.

<sup>18</sup> H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

<sup>19</sup> D. N. Batchelder and R. O. Simmons, J. Chem. Phys. **41**, 2324 (1964).

<sup>20</sup> P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).

is  $648^\circ\text{K}$ . The over-all average velocity appropriate to the specific heat is  $5.93 \times 10^5 \text{ cm/sec}$ .

Another problem in analysis of the data results from the geometrical shape of the samples. In most cases, these were nearly square in cross section with widths  $w_1$  and  $w_2$ , while the Casimir expression applies to a circular cross section of radius  $R$ . Following Casimir, it has been customary to define an effective radius  $R_e$  by

$$\pi R_e^2 = w_1 w_2, \quad (16)$$

and to take

$$l_c = 2R_e = 1.12(w_1 w_2)^{1/2}. \quad (17)$$

We believe, however, that the surface scattering can be better represented by taking  $l_c$  proportional to a harmonic mean rather than a geometrical mean dimension, and thus throughout use

$$l_c = w_{\text{HM}} \equiv 2[w_1^{-1} + w_2^{-1}]^{-1}. \quad (18)$$

For both rectangular and circular cross section,  $l_c$  is then equal to  $4A/P$ , where  $A$  = area,  $P$  = perimeter, and thus coincides with the mean free path for Knudsen flow of a gas.<sup>21</sup> The validity of Eq. (18) will be further discussed later. For purposes of comparing the results with the BSZ theory, we also take the shape factor to be  $l_c/2L$  in place of  $R/L$ , where  $L$  is the total length of the sample including the length within the heater clamps.

## IV. EXPERIMENTAL RESULTS

### A. Rough-Surfaced [111] Rods

Samples of the desired size were cut from the crystal with an abrasive wire saw. "Rough" surfaces were then prepared by lapping with either 600-grit silicon carbide or  $20\text{-}\mu$ ,  $10\text{-}\mu$ , or  $5\text{-}\mu$  aluminum oxide powder.

The size effect of the conductivity is illustrated in Fig. 1 for samples cut from crystal A with rod axis in the [111] direction and nearly square cross section. As noted previously, the faces are of {110} and {112} types. It is seen that the measured conductivity increases roughly as  $T^3$  and as the sample width, so that the qualitative features of the theory are borne out. A more quantitative comparison is given in Table II, where the results on all samples of the present category are collected. It is seen that the exponent in the temperature dependence tends to be slightly less than 3.0, especially for samples lapped with the finer grits. Since the specific heat goes accurately as  $T^3$  in this range, this conductivity behavior can only be due to a slight temperature dependence of the mean free path. The latter could in principle result from either some specularly in the surface scattering or some contribution from bulk scattering. However, neither of these effects appears to be present. At the lower temperatures, where specularly would be more likely owing to the longer

<sup>21</sup> S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley & Sons, Inc., New York, 1962), 2nd ed., p. 87.

average phonon wavelength, the "measured" mean free path is very close to the Casimir value when  $\langle v \rangle_2$  and Eq. (18) are used to compute  $l$  and  $l_c$ , respectively. Obviously, the use of  $\langle v \rangle_1$  and/or Eq. (17) would make  $l/l_c < 1$ . This would be possible only if there were appreciable bulk scattering. But then  $l/l_c$  should be strongly size dependent, whereas it is observed to be almost constant over the 7.5:1 range of  $l_c/2L$  values investigated. The *slight* size dependence predicted by the BSZ theory does appear to be present but is difficult to verify. A further argument against bulk scattering is that sample C1-A (run No. 85 in Table II), which was cut from the apparently purer crystal C, gave results entirely comparable with the others.

Of special note in Table II is run 83. The sample here was cut with a hexagonal cross section, so that all rod faces were of  $\{110\}$  type. Good agreement with the other  $[111]$  rod results was obtained, showing that the rough  $\{110\}$  and  $\{112\}$  surfaces scatter phonons equally well. It is worthy of note that even though the cross section is somewhat close to circular, the agreement was improved by taking  $l_c$  as  $4A/P$  so as to be constant with Eq. (18).

### B. Rough-Surfaced $[100]$ and $[110]$ Rods

Samples with a  $[100]$  rod axis were cut from crystals B and C, some with  $\{100\}$  and some with  $\{110\}$  faces exposed. The results are summarized in Table III. The temperature dependence for most of these samples lies closer to  $T^{2.9}$  than to  $T^{3.0}$ , but this probably results

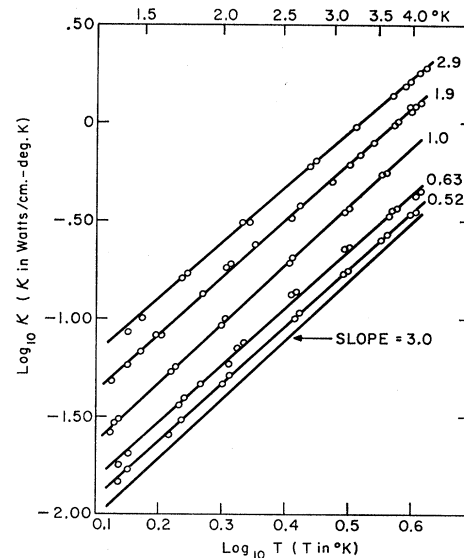


FIG. 1. Thermal conductivity of square rough-surfaced  $[111]$  rods. Curves are labelled with rod widths in mm.

from lapping with a fairly fine grit. There is no essential difference in the value of  $l/l_c$  between samples from crystals B and C, or between samples with the different exposed faces. Most strikingly, however, the values of  $l/l_c$  for the  $[100]$  rods lie distinctly higher than for the  $[111]$  rods. Run 85, previously discussed and listed in Table II, rules out the possibility that some difference in the crystals is responsible. The effect must, therefore,

TABLE II. Summary of results for rough-surfaced samples with  $[111]$  rod axis.<sup>a</sup>

Run	Sample	Lap	$l_c$ , cm	$\frac{l_c}{2L}$	$\frac{d \log_{10} \kappa}{d \log_{10} T}$	$l/l_c$	
						3°K	1.5°K
20 and 21	A1-1A	10 $\mu$	0.217	0.053	2.95	0.96	0.97
43	A1-5A	10 $\mu$	0.100	0.0156	3.00	1.09	1.09
44	A1-6A	10 $\mu$	0.052	0.0071	2.90	0.99	1.07
47	A1-7A	10 $\mu$	0.055	0.0110	2.96	1.00	1.04
48	A1-8A	10 $\mu$	0.064	0.0077	2.96	1.03	1.08
51	A1-10A	5 $\mu$	0.286	0.0339	2.70	0.85	1.02
83	A1-13A	5 $\mu$	0.199	0.0236	2.88	0.93	0.96
97	A1-15A	No. 600 SiC	0.087	0.0112	2.93	0.88	0.91
85	C1-1A	No. 600 SiC	0.095	0.0197	2.94	0.98	1.02

<sup>a</sup> Lapping compound is  $Al_2O_3$ , unless otherwise specified.

TABLE III. Summary of results for rough-surfaced samples with  $[100]$  rod axis.<sup>a</sup>

Run	Sample	Lap	$l_c$ , cm	$\frac{l_c}{2L}$	$\frac{d \log_{10} \kappa}{d \log_{10} T}$	$l/l_c$	
						3°K	1.5°K
57	B2-2-2A	10 $\mu$	0.082	0.0109	2.90	1.50	1.60
72	C2-2-3A	5 $\mu$	0.071	0.0080	2.92	1.58	1.70
75	C2-3-3A	5 $\mu$	0.071	0.0105	2.90	1.57	1.69
76	B2-3-5A	5 $\mu$	0.082	0.0099	2.88	1.54	1.70
78	C2-3-5A	5 $\mu$	0.195	0.0241	2.84	1.35	1.49
84	B2-3-5B	No. 600 SiC	0.069	0.0082	2.96	1.49	1.53
94	C2-3-3C	10 $\mu$ and annealed	0.071	0.0140	2.94	1.47	1.51

<sup>a</sup> Lapping compound is  $Al_2O_3$ , unless otherwise specified.

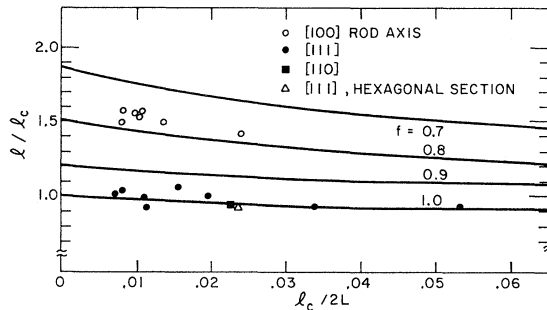


FIG. 2. Comparison of thermal conductivities of rough-surfaced rods with BSZ theory.

be entirely an orientational one. It is of a peculiar nature, however, since the rod axis, not the surface normal, is the significant direction. This is borne out most clearly by a comparison of run 83 (Table II, hexagonal rod) with runs 75, 76, 78, 84, and 94 (Table III); all of these samples had only  $\{110\}$  faces, but the conductivities are quite different.

One run (run 90) was made on a sample cut from crystal C with a  $[110]$  rod axis and pairs of  $\{100\}$  and  $\{110\}$  faces. The value of  $l/l_c$  agreed with the  $[111]$  rods even though the faces are the same as those on the  $[100]$  rods. This further confirms the significance of the rod axis orientation.

The sample of run 94 was annealed in  $N_2$  at  $1230^\circ\text{C}$  for 4 h. This was intended as a further test for bulk scattering. As is seen, no significant changes occurred.

The foregoing results are summarized in Fig. 2, where the  $l/l_c$  values are compared with the BSZ theory. It is seen that the points tend to fall along lines of constant "diffuseness," with  $f=1.0$  for the  $[111]$  and  $[110]$  rods and about 0.77 for  $[100]$  rods. It must be emphasized again that  $\langle v \rangle_2$  was used in obtaining these results. Had  $\langle v \rangle_1$  been used, the  $[100]$  points would be much higher, since the actual conductivity is about double that of a comparable  $[111]$  rod. This raises the question of whether some other more accurate formula for  $\langle v \rangle$  would fully account for the higher  $[100]$  conductivity. A glance at the mode velocities in Table I discloses that this is most unlikely: the transverse modes, which account for about 80% of the conductivity, are simply too nearly isotropic to permit such a range of variation. Thus, the conclusion seems inescapable that acoustic phonons traveling in directions near  $[100]$  are reflected with appreciable specularly even from rough surfaces.

TABLE IV. Summary of results for samples of rectangular cross section.

Run	$w_1/w_2$	$l(3^\circ\text{K})(\text{cm})$	$(w_1w_2)^{1/2}(\text{cm})$	$w_{\text{HM}}(\text{cm})$
40	3.9	0.121	0.144	0.117
86	6.5	0.0840	0.177	0.0790
98	7.3	0.0968	0.146	0.0963
93 and 99	9.2	0.0818	0.118	0.0709

### C. Rough Samples of Rectangular Section

The samples discussed heretofore were all nearly square in cross section. In order to substantiate the use of Eq. (18) for the Casimir length, four additional samples were run whose ratios of widths ( $w_1/w_2$ ) varied from 4/1 to 9/1. All these samples were cut from crystal A, with the rod axis in the  $[111]$  direction and with the face of greater width in the  $\{110\}$  direction. All faces were lapped with either  $20\text{-}\mu$  or  $10\text{-}\mu$   $\text{Al}_2\text{O}_3$  lapping compound, so that we could confidently assume completely diffuse scattering. Comparison of the measured value of  $l$  with  $w_{\text{HM}}$ , and  $(w_1w_2)^{1/2}$  is given in Table IV. It is seen that the geometric mean is really quite inappropriate, and that the harmonic mean does seem correct.

However, most unexpectedly, the log plot of the conductivity versus the temperature turned out not to be linear below  $1.7^\circ\text{K}$ , as illustrated in Fig. 3. Two checks were made on this effect: First, in run 97, the conductivity of a sample of square cross section was again measured, and found to follow a simple power law over the entire range, thus ruling out any possible change in thermometry. Second, run 99 is a repeat of the sample of run 93, except that the distance between the thermometer clamps was changed from 2.66 to 1.43 cm. No difference was found in the measured value of the conductivity, so that the effect is not a result of special changes in the temperature distribution near the ends of the sample. The departure from a simple power law is about 20% at  $1.3^\circ\text{K}$ .

### D. Smooth Surfaces

Smooth surfaces, which diffusely scatter only a fraction of the incident phonons, were prepared by mechanical polishing, chemical etching, and combined chemical-mechanical polishing. Mechanical polishing was done with  $6\text{-}\mu$  and  $1\text{-}\mu$  diamond polishing compound, using

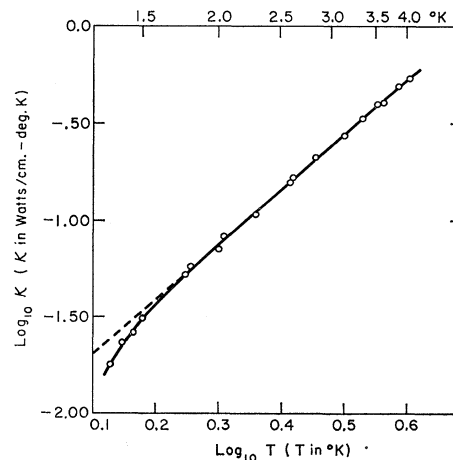


FIG. 3. Thermal conductivity of a rectangular rough-surfaced  $[111]$  rod, of width ratio 9:1 (run No. 93 in Table IV).

an oil lubricant. To minimize the rounding of the edges, the polishing cloth was replaced by a single layer of lens tissue on a plate glass backing. A great deal of practice was required to develop this technique, and even then only rarely could all sides of a crystal be well matched in appearance. Still smoother surfaces were obtained by further polishing the best 1- $\mu$  diamond surfaces with "Lustrox,"<sup>22</sup> which is a suspension of a fine abrasive in a medium that slowly attacks silicon. Here again, much practice was needed to develop optimum technique. Three of the very smoothest surfaces polished with Lustrox were examined with an electron microscope, using a replica method. Except for a few isolated flaws that served to focus the microscope, most of the surface is characterized by large areas with no visible structure within the resolution of the replica. Some samples were also prepared for examination by electron diffraction, which was kindly carried out by Dr. C. F. Tufts of the General Telephone and Electronics Laboratories, Inc., Bayside N. Y. Although the results were somewhat variable, the best samples showed a rather high degree of perfection as evidenced by well-defined spots and Kikuchi lines. Polishing was also done with the chemical etch CP4-A.<sup>23</sup> However, as the etching rate was strongly dependent upon the rate of stirring, reproducible results were difficult to obtain.

Some results for samples polished with 1- $\mu$  diamond and with Lustrox are shown in Fig. 4. Of the two Lustrox-polished samples, run 70 is a fairly typical one and run 63 is one of the two very smoothest surfaces obtained. The temperature dependence is much less than  $T^3$ , indicating that the phonon mean free path  $l$  is now strongly temperature-dependent. This is undoubtedly a consequence of the temperature dependence of the phonon-wavelength distribution since one would expect phonons to be scattered specularly whenever the surface imperfections are roughly smaller in size than their wavelength. It is also seen that for the smooth surfaces the log plot of the thermal conductivity versus the temperature is no longer linear, the deviation becoming more severe as the smoothness improves.

The results for all samples with 1- $\mu$  diamond polishes are given in Table V. The values of  $l/l_c$  scatter about the curves of constant diffuseness  $f$  in the BSZ theory. This probably reflects surface variations from the 1- $\mu$

TABLE V. Summary of results for 1- $\mu$  diamond-polished surfaces.

Run	Sample	$l_c$ , cm	$l_c$	$\frac{d \log_{10} \kappa}{d \log_{10} T}$	$(l/l_c)$	
			$2L$	$d \log_{10} \kappa$	3°K	1.5°K
67	A1-12A	0.093	0.0110	2.08	2.49	4.63
55	B2-2-1A	0.085	0.0092	2.28	3.54	6.50
59	B2-3-1A	0.087	0.0105	2.24	3.66	6.23
64	C2-2-1A	0.083	0.0093	2.06	3.98	7.32

<sup>22</sup> Trade name of product of Tizon Chemical Corp., Flemington, N. J.

<sup>23</sup>  $5\text{HNO}_3:3\text{HF}:2\text{CH}_3\text{COOH}$ .

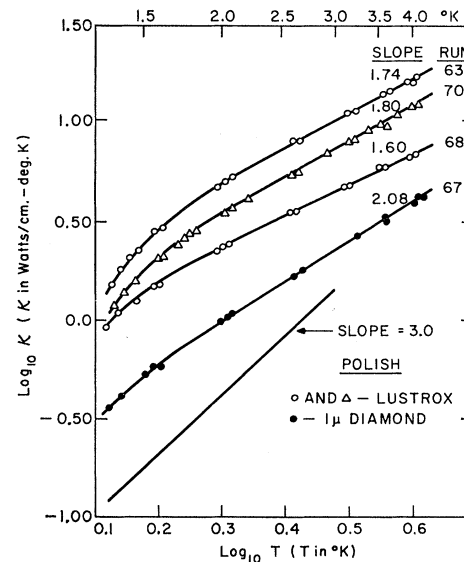


FIG. 4. Thermal conductivity of various polished samples.

polishing, since optical examination of the surfaces revealed a wide range of surface textures. Therefore, any comparison between samples of different rod axes or rod faces is not too meaningful, although the value of  $l/l_c$  obtained for the sample with the  $[111]$  rod axis is somewhat lower than the samples with a  $[100]$  rod axis, as was true of the rough surfaces.

Surfaces polished with Lustrox can be divided into three groups of relative smoothness, which we shall term "poor," "good," and "outstanding." The poor surfaces, when observed through an optical microscope using Nomarski (interference contrast) illumination, had a pebbled texture with many grooves resulting from poor diamond polishing technique, and often were pitted from too long an exposure to the Lustrox. There were four of these samples, measured in runs 52, 60, 61, and 77. The poorest of these had the same conductivity as when polished to the 1- $\mu$  diamond stage. Generally, however, the conductivity was increased even with a poor Lustrox polish.

Seven samples with good Lustrox surfaces showed reasonable consistency in the smoothness of the surface as determined by the conductivity. This is shown in Fig. 5, where the values of  $l/l_c$  at 3 and 1.5°K are plotted on the BSZ curves. The values of  $l/l_c$  at 3°K do not lie quite parallel to the curves of constant diffuseness but at 1.5°K they lie almost on the  $f=0.10$  curve. (It will be noted that the conductivity is highly sensitive to  $f$  for small  $f$  values, and therefore that considerable variation about the constant- $f$  curves is to be expected.) All points are for samples with rod axes in the  $[100]$  direction with the exception of one of the lower points, which is for the  $[111]$  rod axis. Five of these samples had widths of about 0.9 mm, one had a width of 1.80 mm, and the remaining one a width of 0.467 mm. Handling of the very thin sample was quite precarious,

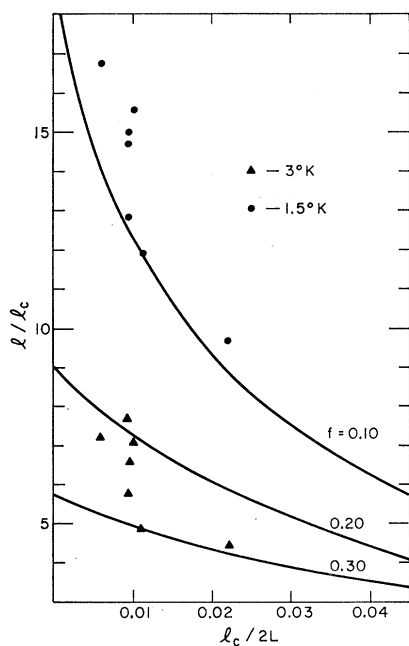


FIG. 5. Comparison of thermal conductivities of Lustrox-polished rods with BSZ theory.

and samples of still smaller cross sections were not attempted.

The results in Fig. 5 are for different samples, and it is still possible that the variation in the conductivities is not a result of the size effect but rather a result of differences in surface polishing. Therefore, a single sample from the above group was progressively shortened in length to increase the value of  $l_c/L$ . The results are shown in Fig. 6 and give entirely satisfactory agreement with the BSZ theory.

Two samples produced exceptionally long phonon mean free paths. The conductivities of these samples of outstanding smoothness were measured in runs 63 and 71. These surfaces are by far the smoothest ever reported, with values of  $l/l_c$  at 1.5°K about 30% above the  $f=0.10$  curve in Fig. 6. The results are listed in Table VI which also includes results of the samples with

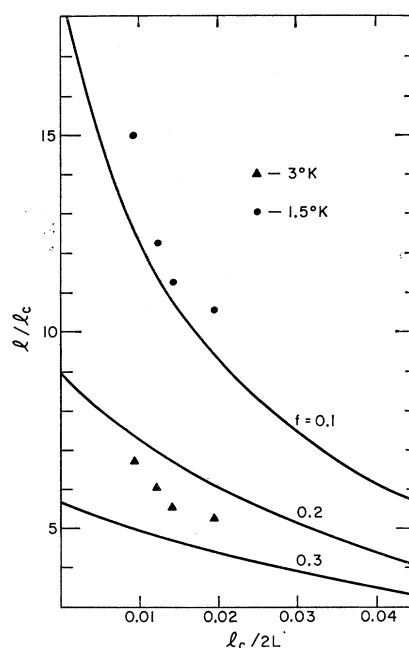


FIG. 6. Comparison of thermal conductivity of a single Lustrox-polished rod with BSZ theory. Rod was polished once then progressively shortened. Sample C2-3-1, runs 73, 87, 88, and 89 of Table VI.

good Lustrox surfaces. On examination with the optical microscope, the surfaces of good and outstanding smoothness were both almost featureless, and any surface texture that existed was on the very edge of detection. In view of the difference in diffuseness  $f$  obtained, we conclude that the smoothness of a surface cannot be characterized sufficiently well by optical examination so that meaningful comparison between different rod axes or rod faces can be made.

Table VI also indicates that there is a limit to the increase in the mean free path with decreasing temperature, reached at about 1.5°K. This is reflected in the downward curvature illustrated in Fig. 4, as if the conductivity were returning to a  $T^3$  dependence. Since the mean free path is then reaching some temperature-

TABLE VI. Results for surfaces polished with Lustrox.

Run	Sample	$l_c$ , cm	$\frac{l_c}{2L}$	$\frac{d \log_{10} \kappa}{d \log_{10} T}$	$(l/l_c)$						
					4°K	3°K	2°K	1.7°K	1.5°K	1.4°K	1.3°K
63	B2-3-3A	0.0876	0.0103	1.72	6.81	9.84	16.5	18.7	20.0	19.9	19.4
71	C2-2-2A	0.083	0.0093	1.70	5.36	7.81	13.5	16.2	18.9	18.4	18.8
70	B2-3-4A	0.085	0.0094	1.80	5.58	7.76	12.9	13.8	14.8	15.3	15.2
68	A1-12A	0.0934	0.0110	1.60	3.26	4.95	8.75	10.8	11.9	12.2	12.6
66	C2-2-1B	0.083	0.0093	1.82	4.04	5.77	9.57	11.3	12.8	12.8	...
73	C2-3-1A	0.0834	0.0098	1.76	4.85	6.76	11.4	13.9	15.0	15.3	15.4
74	C2-3-2A	0.0794	0.0101	1.76	5.21	7.12	12.0	14.6	15.8	16.1	16.3
79	C2-3-4B	0.0467	0.0059	1.80	5.10	7.28	11.7	14.4	16.8	17.1	17.9
82	C2-3-5B	0.180	0.0222	1.88	3.16	4.43	7.16	8.45	9.63	10.5	11.3
87	C2-3-1B	0.0834	0.0122	2.00	4.53	6.04	9.09	10.7	12.2	13.1	...
88	C2-3-1C	0.0834	0.0144	1.86	3.95	5.52	8.70	10.5	11.3	11.8	...
89	C2-3-1D	0.0834	0.0195	1.86	3.76	5.36	8.48	10.3	10.6	11.1	...



TABLE VII. Summary of results for surfaces chemically etched with CP4-A.

Run	Sample	Polish prior to etch	Etch time (sec)	$l_c$ -cm	$l_c$	$d \log_{10} \kappa$	$(l/l_c)$	
					$2L$	$d \log_{10} T$	3°K	1.5°K
54	A1-11C	Lustrox	60	0.052	0.012	2.58	1.72	2.34
58	B2-2-1C	Lustrox	30	0.086	0.0010	1.90	4.74	9.96
62	B2-2-1E	Lustrox	30	0.085	0.010	2.12	3.52	6.24
50	A1-9B	30-sec etch	30	0.050	0.0092	2.34	2.20	3.52
45	A1-5B	1- $\mu$ diamond	60	0.085	0.013	1.90	3.05	6.29
46	A1-5C	30-sec etch	120	0.079	0.012	2.40	1.90	2.88

independent value, the question is raised as to what the remaining scattering mechanism might be, and whether it is connected with the bulk or the surface. The fact that two surfaces smoother than the good Lustrox-polished ones could be prepared suggest that the mechanism is still a surface effect. It would be very desirable to extend these measurements below 1.3°K, to determine if the conductivity does maintain a  $T^3$  dependence for the smooth surfaces.

Seven samples were run with surfaces chemically etched with CP4-A. The results are summarized in Table VII. Since the rate of etching is strongly dependent upon the stirring of the bath, the constant time for different samples does not imply that the etches have the same effect. Changes in sample width in a 30-sec etch varied from 1.4 mil to less than 0.1 mil. Surfaces prior to etching were polished either to the 1- $\mu$  diamond stage or with Lustrox. In all cases etching of the surface decreased the conductivity. Therefore, efforts to produce smoother surfaces with chemical etching were not pursued any further. Optical examination of the surfaces revealed surface changes upon etching ranging from barely perceptible differences in surface texture to surfaces of entirely different character.

One of the very smoothest surfaces was argon-bombarded and -annealed. The bombarding and annealing schedules approximated those used by Forman<sup>24</sup> in the preparation of clean germanium surfaces, namely, a current density of 50  $\mu$ A/cm<sup>2</sup>, with a bombarding voltage of 500 V at an argon pressure of  $15 \times 10^{-3}$  Torr for 20 min. Thermal-conductivity measurements were made, and then the sample was annealed in a  $2 \times 10^{-5}$  Torr vacuum for 20 h at 475°C after outgassing for 2 h at 650°C. Results of the conductivity measurements are shown in Fig. 7. The sample had a [100] rod axis, and exposed the {110} rod faces. The conductivity decreased after bombardment, and decreased even further after annealing. If the annealing had improved the surface perfection, one would have expected the conductivity to increase over its bombarded value. The decrease might be a result of poor design of the annealing apparatus, as the heated sample was only a few centimeters above a glass plate. Allen *et al.*<sup>25</sup> have shown that silicon crystals heated in glass vacuum

systems can become heavily doped to a depth of several microns. Further, Holland and Neuringer<sup>26</sup> have shown boron to be particularly effective in scattering phonons in silicon. The sample surfaces were examined under the microscope before and after bombarding and annealing. No detectable change in the surface was observed after the bombardment. However, after annealing, one side of the sample showed many slip lines, mostly in the (111) direction, although there were some in the (100) direction. The other three surfaces of the crystal showed no observable changes after annealing. These experiments were not carried any further. However, it is clear that ion bombarding and annealing results in surface changes which show up quite dramatically in the thermal conductivity, and experiments measuring the conductivities of samples with varying bombarding and annealing schedules, could be quite revealing.

## V. DISCUSSION

Probably the most remarkable result of the present investigation is the orientation-dependent partial

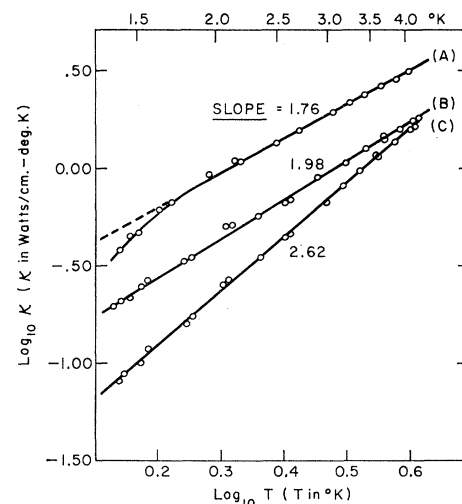


FIG. 7. Effects of argon ion bombardment and annealing on a Lustrox-polished sample. Curve A, run 74, as polished; B, run 95, bombarded; C, run 96, annealed.

<sup>24</sup> R. Forman, Phys. Rev. **117**, 698 (1960).

<sup>25</sup> F. G. Allen, T. M. Buck, and J. T. Law, J. Appl. Phys. **31**, 979 (1960).

<sup>26</sup> M. G. Holland and L. J. Neuringer, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 475.

specularity of the rough surfaces. There are really two questions involved here: How can such very rough surfaces be at all specular, and how can this depend on the heat-flow direction but not the surface orientation?

With regard to the first, it is noteworthy that Thacher<sup>8</sup> observed the same effect in his careful studies on isotopically pure LiF; the sand-blasted samples had a conductivity some 25% higher than expected from the BSZ theory. Thatcher used a direction-averaged value of velocity, but this differs by only a few percent from the value of  $\langle v \rangle_2$  for the [100] direction that he studied, and thus cannot account for the discrepancy. Thacher gives much consideration to a dislocation scattering mechanism, and cites some experiments that tend to substantiate it. This may well explain why diffuse scattering occurs in an apparently smooth crystal, but quite obviously cannot account for the opposite effect. Since the surfaces we are discussing are rough on a scale of optical wavelengths, which are more than ten times the dominant phonon wavelengths, the obvious explanation within the existing theoretical framework is that some phonons never really encounter the surface at all but are "refracted" away by a subcutaneous stress field. Some credibility is lent to this idea by the observation that chemical etching can lower the conductivity of a diamond-polished crystal; this could be due to a stress-relief effect. It is also possible though, that the entire theory needs a thorough reworking. When this is done, due attention should be given to such questions as the distinction between "diffuse reflection" on the one hand and "absorption and reemission" on the other, and the possible angle dependence of the specularity factor. The problem should be set up in rectangular geometry so that the deviation from  $T^3$  behavior in the nonsquare samples can also be investigated.

With regard to the orientation effect, it is interesting to note that this was actually foreshadowed in earlier observations on Si. This is seen in a comparison of the conductivity measured on a [111] rod by Glassbrenner and Slack<sup>5</sup> with that measured on a thinner [100] rod

by Carruthers *et al.*<sup>27</sup> In any case, the effect was most surprising. One conceivable explanation is that the specular reflection (or refraction) is somehow connected with the propagation of Rayleigh waves. In this connection Gazis *et al.*<sup>28</sup> find that, for directions in the {001} plane, propagation is fully allowed in the vicinity of [100], where we observe partial specularity, and excluded in the vicinity of [110], where we observe complete diffuseness. Admittedly, this connection is somewhat tenuous, but nothing better suggests itself.

In connection with the smooth surfaces, the only remaining remark is that it is surprising that the BSZ size-effect theory works as well as it does (cf. Fig. 6). When the diffusivity factor becomes as small as 0.1, the underlying assumptions such as local equilibrium, planar isothermal surfaces, etc., become somewhat dubious. Apparently, though, the effects are not serious until even higher specularity is reached.

#### ACKNOWLEDGMENTS

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<sup>27</sup> J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, Proc. Roy. Soc. (London) **A238**, 502 (1957).

<sup>28</sup> D. C. Gazis, R. Herman, and R. F. Wallis, Phys. Rev. **119**, 533 (1960).