Ratio of the Lattice Thermal Conductivities of Normal and Superconducting Indium*

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Measurements are reported of the thermal conductivity of ten specimens of indium with small amounts of tin and bismuth, with residual resistivities between 0.12 and 6 $\mu\Omega$ cm. The normal-state lattice conductivity shows the characteristic variation with electronic mean free path previously reported for other metals. The ratio of the lattice conductivities in the superconducting and normal states in the region where electron scattering predominates is in reasonable agreement with the theoretical predictions of Bardeen, Rickayzen, and Tewordt.

SINCE the development of the microscopic theory of superconductivity, there has been renewed interest in measurements of the thermal conductivity of superconductors. There have been several investigations of the ratio of the electronic conductivities in the superducting and normal states, but information on the ratio of the lattice components has been scarce and inconclusive.

In the normal state of pure metals the lattice conductivity is too small a fraction to be detectable. If the electronic mean free path is decreased by the addition of impurities, both kinds of heat carriers will suffer increased scattering, but the lattice conductivity decreases more slowly, so that it becomes a larger (and therefore more easily measurable) fraction of the total conductivity. The main problem is to separate the two components, and to distinguish between the effects related to the impurities and those intrinsic to the pure metal.

We have made measurements on ten specimens of indium with small amounts of either tin or bismuth in the normal and superconducting states. We find that in the normal state the change of the lattice conductivity with electronic mean free path is similar to that found in other metals. We also find that the ratio of the lattice conductivities is in reasonable agreement with the theoretical predictions.

EXPERIMENTAL RESULTS

The specimens were made of 99.999% pure tin (Vulcan Detinning Company), indium, and bismuth (American Smelting and Refining Company). They were cast under vacuum in Pyrex tubes coated with Aquadag to avoid adhesion. They were about 3 mm in diameter, 2 to 3 cm between thermometers, and were annealed near the melting point for at least two weeks. Table I shows their characteristics.

The measurements were made in an apparatus described previously.[1] To obtain the normal state below the superconducting transition temperature T_c a water-cooled Helmholtz coil capable of providing about 3000 G was used.

The scatter of the measured conductivities indicates a precision of about $\frac{1}{4}$% for each specimen. The absolute accuracy is limited by the uncertainty in the geometrical factor, and is estimated to be about 2%.

The variation of the normal state conductivity K_n with temperature is shown on Fig. 1 as K_n/T against T. Before discussing the details of the analysis we describe some of the main features of this set of curves.

The thermal conductivity is in each case dominated by impurity scattering, which would lead to a horizontal line on the figure. In the range of our measurements the other contributions change the conductivity from 3% in the purest specimen (In 1) to 20% in the most impure (In 7).

There are several competing factors, the relative magnitude of which depends on the purity of the specimens. The lattice conductivity accounts for the upward trend with increasing temperature. In the purer specimens this trend is masked by the downward trend with temperature caused by the scattering of electrons by phonons. In the more impure specimens containing bismuth the curves are observed to flatten out at the upper end as a result of the reduction of the lattice conductivity by impurity scattering.

TABLE I. Specimen characteristics. Specimens numbered 1 to 7 contain bismuth, specimens 8 to 10 contain tin. (The residual resistivity ρ_0 of indium increases by about 1.8 $\mu\Omega$-cm/% with the addition of bismuth, and about 0.36 $\mu\Omega$-cm/% with the addition of tin.)

	ρ_0 ($\mu\Omega$ cm)	T_c (deg K)	C (W/cm-deg^3)	C' (W/cm-deg^3)
In 1	0.122	3.39		
In 2	0.246	3.39		
In 3	0.460	3.40		
In 4	0.690	3.40	0.70×10^{-3}	0.37×10^{-3}
In 5	2.86	3.69	0.38×10^{-3}	0.20×10^{-3}
In 6	3.63	3.84		
In 7	5.9	4.21		
In 8	2.13	3.90	0.43×10^{-3}	0.23×10^{-3}
In 9	0.308	3.42		
In 10	0.530	3.44	0.65×10^{-3}	0.43×10^{-3}

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[1] P. Lindenfeld and W. B. Pennebaker, Phys. Rev. **127**, 1881 (1962).

The scattering of phonons by impurities is expected to depend to a large extent on the mass difference between the host and impurity atoms, and should therefore be much stronger in the specimens containing bismuth. The effect may be illustrated by a comparison of the conductivities of specimens containing tin and bismuth, respectively, with similar residual resistivities, i.e., with similar values of the electronic mean free path. If we compare a pair of fairly impure specimens, such as In 5 and In 8, we see that the conductivity of In 5 (which contains bismuth) is lowered at the higher temperatures because of the scattering of phonons by bismuth atoms. For a pair of purer specimens, such as In 2 and In 9, the curves are similar, indicating that effects are small. In these two specimens the lowering of the conductivity at the higher temperatures must therefore be ascribed to the scattering of electrons by phonons.

Figure 2 shows the ratio R of the thermal conductivity in the superconducting state (K_s) to that in the normal state (K_n) as a function of the reduced temperature $t=T/T_c$. In the purer specimens, R drops with decreasing temperature as the energy gap increases and more and more electrons are removed from the thermal-conduction process. At the same time the electrons are removed as scatterers of the phonons so that the lattice conductivity becomes larger. In the most impure specimens the increase of the lattice conductivity is more important than the decrease of the electronic

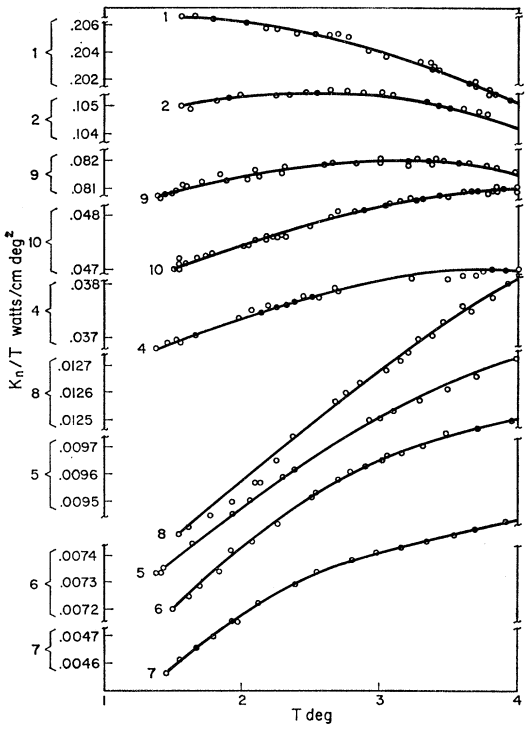

FIG. 1. The normal-state lattice conductivities plotted as K_n/T against T for all specimens except In 3.

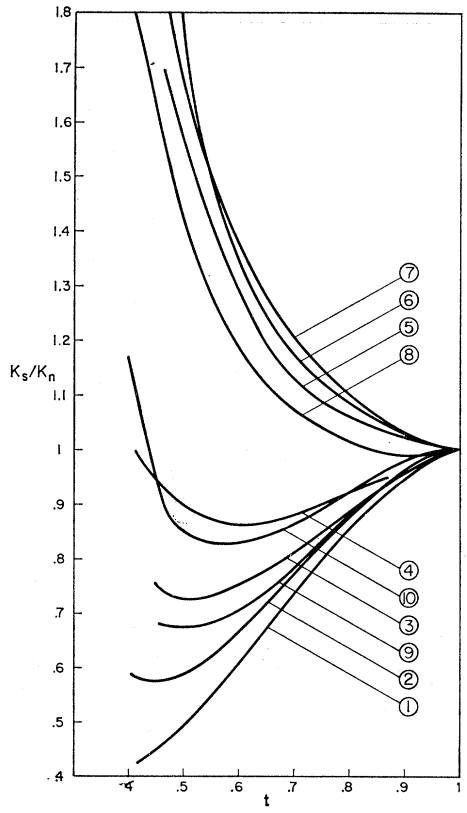

FIG. 2. The ratio of the measured total conductivities in the superconducting and normal states as a function of the reduced temperature.

conductivity, and the ratio increases as the temperature is lowered. For intermediate cases R decreases at first, and then increases.

At the low end of our temperature range we are approaching the region where the boundary scattering of phonons becomes important. At still lower temperatures the lattice-conductivity ratio passes through a maximum, since it must decrease with decreasing temperature when boundary scattering predominates. For any given combination of the other scattering mechanisms the height of the maximum and the temperature at which it occurs will be greatest for the largest boundary mean free path. It is usually found that the purer specimens have larger subgrains and correspondingly larger boundary mean free paths as determined by the internal as well as the external boundaries. Thus the total conductivity ratio curves for different specimens may cross. Two examples of this behavior are seen in Fig. 2.

ANALYSIS OF RESULTS

Our object is to deduce information about the ratio of the lattice conductivities $R_g \equiv K_{gs}/K_{gn}$ from the measured conductivities K_s and K_n in the superconducting and normal states, and from our prior knowledge of

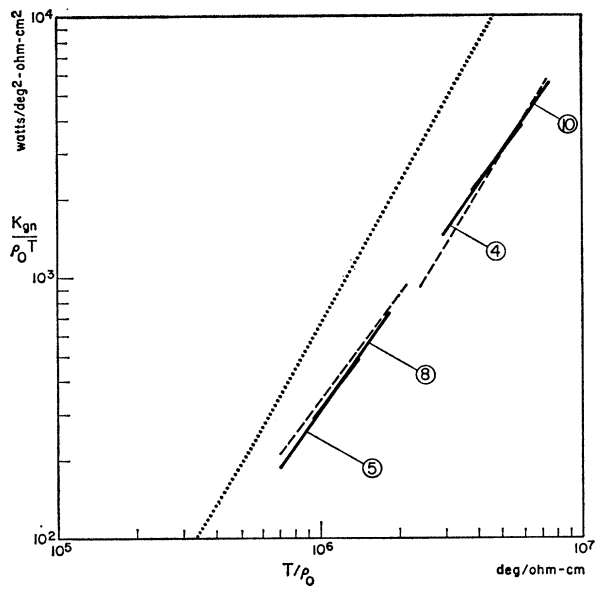

FIG. 3. Graph of $K_{gn}/\rho_0 T$ against T/ρ_0. (K_{gn} is the normal-state lattice conductivity and ρ_0 is the residual electrical resistivity). The dotted line is the theoretical curve from Ref. 1, scaled to apply for indium. The full lines are for $K_{gn}=C'T^{2.4}$ with C' from Table I. The dashed lines are for two of the copper specimens of Ref. 1 scaled as described in the text.

the ratio of the electronic conductivities, $R_e \equiv K_{es}/K_{en}$. Ratio functions similar to R_e and R_g were introduced by Hulm,[2] who observed that they were, to a good approximation, universal functions of the reduced tem-temperature. We first separate the normal-state conductivity K_n into its contributions K_{en} and K_{gn} with the help of our knowledge of the temperature dependence of the separate terms. We can then calculate R_g from the relation $R_g=(K_s-R_eK_{en})/K_{gn}$.

Electronic Conductivity

The ratio R_e has been described by Bardeen, Rickayzen, and Tewordt[3] (BRT) for the case where impurity scattering is the only significant mechanism, and by others[4] for the case where phonon scattering is appreciable. Since phonon scattering is small in all our specimens the BRT results are expected to apply.

The BRT relation for R_e is a function of the parameter $\epsilon(T)/kT$. For $2\epsilon(0)/kT_c$ we have used the value 3.7 which has been shown to be appropriate for indium, and unchanged by the addition of several percent of tin.[5]

For the electronic conductivity we use the expression

$$1/K_{en}=A/T+BT^2, \qquad (1)$$

where the first term represents the resistance caused by impurities and imperfections and the second that caused by phonons. The coefficient B becomes larger as the electronic mean free path decreases,[6] but more slowly than the coefficient A. The second term in Eq. (1) is therefore more important in the purer specimens, where it represents a greater fraction of the resistance. Even in our purest specimen (In1), however, it reduces the conductivity by less than 6% in the range of our measurements. In specimens In2, In3, and In9 the reduction in the electronic conductivity is masked by a lattice conductivity of roughly equal magnitude, and the two are difficult to separate. Precise measurements to higher temperatures might make it possible to distinguish the two contributions, and to extend our knowledge of the variation of the scattering of electrons by phonons with electronic mean free path. For the present we can only say that our measurements are consistent with those of Ref. 6.

Lattice Conductivity: Normal State

We now focus our attention on the next four specimens in order of decreasing electronic mean free path, In10, In4, In8, and In5, in which the scattering of electrons by phonons is expected to play only a small role. We use the results for these specimens to gain information on K_{gn}, with the expectation that for them the lattice conductivity will be determined primarily by the scattering of phonons by electrons. We leave out of consideration, for the moment, specimens In6 and In7, where K_{gn} is lowered appreciably by impurity scattering.

Within the accuracy of our measurements the curves of Fig. 1 for In10, In4, In8, and In5 can be fitted by straight lines over a substantial part of the temperature range, corresponding to an electronic conductivity T/A and a lattice conductivity CT^2. Near the upper end of our temperature range the lines bend over, as a result of the scattering of electrons by phonons, and of phonons by impurities. The values of C estimated from the straight line portions (with small allowances for the second term in Eq. 1) are shown in Table I. The magnitudes of the coefficients C and their dependence on the electronic mean free path are in good agreement with the results of Sladek[7] on a series of indium-thallium alloys.

For the specimens under consideration the electronic mean free path is considerably greater than the wavelength of the dominant phonons. The conductivity of the longitudinal phonons is therefore expected to vary as the square of the temperature.[8] For the transverse

[2] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98, (1950).
[3] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1954).
[4] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961); L. Tewordt, Phys. Rev. **128**, 2 (1962); Phys. Rev. **129**, 657 (1963); B. T. Geilikman and V. Z. Kresin, Zh. Eksperim. i Teor. Fiz **41**, 1142 (1961) [English transl.: Soviet Phys.—JETP **14**, 816 (1962)].
[5] T. B. Greenslade, Jr., P. Lindenfeld, and B. Serin, Bull. Am. Phys. Soc. **10**, 44 (1965).
[6] A. M. Toxen, G. K. Chang, and R. E. Jones, Phys. Rev. **126**, 919 (1962).
[7] R. J. Sladek, Phys. Rev. **97**, 902 (1955).
[8] A. B. Pippard, Phil. Mag. **46**, 1104 (1955); J. Phys. Chem. Solids **3**, 175 (1957).

phonons, however, a more rapid variation with temperature is indicated.[1] It is helpful to plot the lattice conductivity as $K_{gn}/\rho_0 T$ against T/ρ_0 because on such a graph the results for specimens with different electronic mean free paths are expected to lie on a single curve. For $K_{gn}=C'T^n$ the slope of the curve will be $n-1$. If points are plotted on such a graph for the four specimens at a given temperature, they are seen to lie on a line corresponding to $n=2.4$. It now becomes interesting to re-examine the curves of Fig. 1 to see whether they might not be consistent with a lattice conductivity equal to $C'T^{2.4}$. It is found that they are indeed quite consistent with this temperature variation. It should be noted that a fit to the curves of Fig. 1 assuming the more rapid temperature variation leads to slightly larger values of the electronic conductivity, and correspondingly reduced values of the lattice conductivity. Table I includes the values of the coefficient C' obtained from the curves of Fig. 1.

Figure 3 shows a graph of $K_{gn}/\rho_0 T$ against T/ρ_0. The lattice conductivities for specimens In4, 5, 8, and 10 were calculated from the values in Table I, with $K_{gn}=C'T^{2.4}$. As described in Ref. 1, the coordinates of the graph of Fig. 3 will be independent of the specimen material if the ordinate is multiplied by $(b^{2/3}/A\theta)$ and the abscissa by $(b^{2/3}n^{1/3}\theta)^{-1}$, where b is the valence, A the atomic weight, θ the Debye temperature, and n the number of atoms per unit volume. In order to compare results for different materials the ratios of these scaling factors must be used (i.e., a graph of $K_{gn}/\rho_0 T$ against T/ρ_0 for copper may be plotted on Fig. 3 if the ordinate is first divided by 3.6 and the abscissa by 1.9). This has been done for the theoretical curve and for two of the experimental curves of Fig. 5 in Ref. 1.

When scaled in this way the experimental curves for indium and copper alloys are remarkably similar. In each case the experimental curve is close to the theoretical curve for low values of T/ρ_0, and falls more and more below it as T/ρ_0 increases.

One reason for the discrepancy might be that longitudinal and transverse waves have been treated quite separately. More realistic calculations have been made by Feldman,[9] taking into account the mixed character of the waves in all directions except along the crystal axes. These calculations show that the error made by treating the modes separately is, at least in copper, quite small.

Another deficiency of the theory is that it is based on a free-electron calculation. Departures from a spherical Fermi surface will lead to increased scattering of the transverse waves, reverting, for sufficiently high values of the ratio of the electronic mean free path to the phonon wavelength, to a temperature dependence like that of the scattering of longitudinal waves.[10] If this were the main reason for the difference between the experimental and theoretical curves, one might expect copper and indium alloys to give different results. Our measurements indicate that differences in the electronic structure of these metals have little influence on their lattice conductivity.

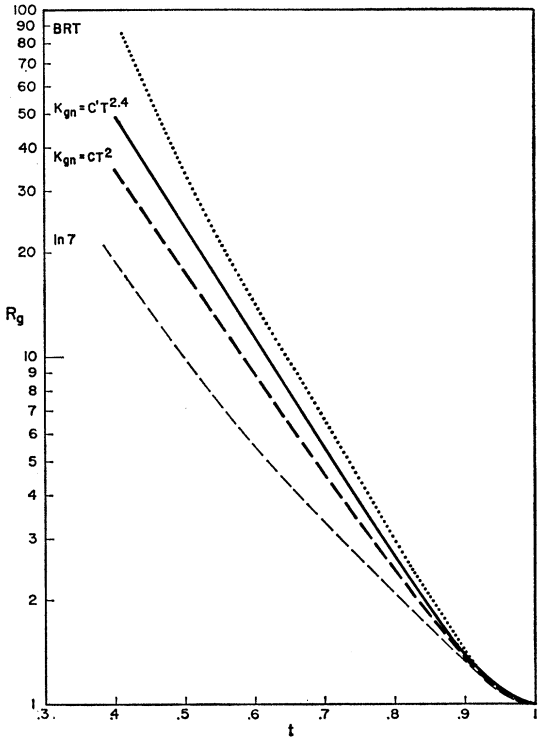

FIG. 4. The ratio of the lattice conductivities in the superconducting and normal states as a function of the reduced temperature. The dotted curve represents the theoretical relation of Bardeen-Rickayzen-Tewordt. The heavy curves are drawn for specimens In 4, 5, 8, and 10; for the full curve we have used $K_{gn}=C'T^{2.4}$ and for the dashed curve $K_{gn}=CT^2$. The thin dashed curve is for the most impure specimen, In 7.

Lattice Conductivity: Ratio

The ratio R_g of the lattice conductivities may now be calculated. We have done this for both sets of possible values, i.e., for a normal state lattice conductivity equal to CT^2, and for one equal to $C'T^{2.4}$. In each case the calculated lattice ratios for the four specimens are so close that they have been averaged before being plotted on Fig. 4. The two curves are seen to be reasonably close to the BRT curve, with the one for a lattice conductivity proportional to $T^{2.4}$ in somewhat better agreement. The BRT curve is calculated for scattering by electrons only, and the presence of other scatterers, such as boundaries and impurities, will serve to decrease R_g. The effect of impurities on R_g has been calculated by Klemens and Tewordt.[11] These authors have shown that the effect of impurities on the lattice condutivity ratio

[9] C. Feldman, following paper, Phys. Rev. **139**, A211 (1965).
[10] A. B. Pippard, Proc. Roy. Soc. (London) **A257**, 165 (1960).
[11] P. G. Klemens and L. Tewordt, Rev. Mod. Phys. **36**, 118 (1964).

TABLE II. The lattice-conductivity ratio R_g as a function of $\epsilon(T)/kT$, for a relaxation time τ inversely proportional to the frequency (see Ref. 13) and for a constant relaxation time. The reduced temperatures t are calculated for $2\epsilon(0)/kT_c=3.7$.

$\epsilon(T)/kT$	R_g $\tau\propto 1/\nu$	R_g τ const	t
0.45	1.011		0.981
0.60	1.034	0.987	0.967
0.80	1.102		0.942
1.00	1.298	1.076	0.914
1.25	1.698		0.872
1.50	2.375	1.741	0.827
2.00	4.933	3.858	0.736
2.67	12.07	10.98	0.620
3.34	27.27	28.39	0.525
3.75	42.86		0.476
4.00	55.89	62.9	0.450
4.34	79.52		0.419
5.87	364.1	430	0.316

can be considerable, even when the effect on the normal state conductivity is small.

For specimens In6 and 7 there is so much impurity scattering that it is not possible to use the same analysis as for the purer specimens. We have instead calculated the lattice conductivity by subtracting the electronic conductivity as calculated from the residual electrical resistivity and the Wiedemann-Franz law. The ratio curve for In7 is shown on Fig. 4. It is seen to fall more and more below the curves for the other specimens as the temperature is lowered.

We are postponing a detailed calculation of the expected deviation of R_g from the BRT curve because we feel that insufficient information is available on two important points. We have made numerical calculations similar to those of Klemens and Tewordt but including a boundary-scattering term. These have shown that the effect of boundary scattering is difficult to distinguish from that of impurity scattering in the temperature range of our measurements. There is evidence that boundary scattering is more important than would be calculated from the size of the crystallites,[12] and we believe that further investigation is needed before reliable estimates can be made. We hope to make measurements at lower temperatures, where boundary scattering predominates, to clear up this question.

The second reason why a more detailed analysis is difficult at this time is the uncertainty in the frequency dependence of the scattering of phonons by electrons. As has been described earlier, measurements of the normal-state lattice conductivity have so far given only rough information of this kind. Another aspect of the same question is the uncertainty of the relative contributions of longitudinal and transverse modes. The dependence on the sound velocity makes the effect of impurities and boundaries very different for the two cases. In fact, the difference is so large that it should be possible to use the dependence of the lattice conductivity on the mean free path to gain information on the contributions of the longitudinal and transverse modes.

In the BRT calculation for R_g it is assumed that in the normal state all phonons have a relaxation time inversely proportional to the frequency. This assumption is appropriate for longitudinal phonons with wavelengths smaller than the electronic mean free path and leads to a lattice conductivity proportional to the square of the temperature. As has been described earlier this assumption may not be appropriate for the transverse phonons. In the limit of long electronic mean free paths the free-electron calculation leads to a constant relaxation time, and a lattice conductivity proportional to the cube of the temperature. We have calculated R_g for this case with the help of intermediate results sent to us by Professor L. Tewordt.[13] The calculated values for R_g are listed in Table II, where, for completeness, we also list Tewordt's values as calculated from the BRT formula. Our normal state results indicate that the lattice ratio appropriate for our specimens should be intermediate between the two sets of Table II. The difference between the ratio expected for our specimens and that calculated for longitudinal phonons is too small to be distinguished by our experiment.

One might expect the interaction of transverse waves and electrons to be quite different in the normal and superconducting states, as a result of the differences in the shielding of magnetic fields in the two states. Calculations by P. R. Weiss[14] show, however, that when the normal skin depth is much larger than the wavelength (as is the case for all our specimens), the shielding is not changed appreciably by the transition.

COMPARISON WITH EARLIER WORK

A comprehensive study of the thermal conductivity of indium-thallium alloys has been made by Sladek.[7] Sladek's results for R_g are consistent with ours and differ chiefly because of differences in the accuracy and analysis of the normal state lattice conductivities. Some of Sladek's specimens were measured down to 0.15°K by Phillips.[12] At the lowest temperatures, the conductivity was proportional to T^3 as expected for boundary scattering. The mean free path corresponding to the coefficient of T^3 was about one tenth of the grain size.

An attempt to find R_g was made by Chang, Jones, and Toxen[6] by assuming one of Sladek's values for K_{gn}. They did not, however, obtain significant information on R_g in the region where boundary and impurity effects are small.

[12] N. E. Phillips, Phys. Rev. **100**, 1719 (1955).

[13] During the preparation of this manuscript we learned from Professor Tewordt that he had made extensive calculations of R_g in connection with the work described in Ref. 11. We used the results of his calculations for Fig. 4 and Table II. We are very grateful to Professor Tewordt for sending us his results and allowing us to use them.

[14] P. R. Weiss (private communication).

A recent determination of K_{gs} for niobium and tantalum was made by Connolly and Mendelssohn.[15] They did not measure K_{gn}, but assumed it to be proportional to T^2 and normalized R_g at $t=0.3$. The temperature dependence was then in accordance with BRT for niobium, and reasonably close for tantalum.

Our measurements extend these investigations of the ratio of the lattice conductivities as limited by electron scattering. We conclude that within the uncertainties of the measurement and of the analysis the experimental results are in agreement with the predictions of Bardeen, Rickayzen, and Tewordt.

The dependence of the scattering of phonons by electrons on the electronic mean free path has been observed in a number of experiments.[16] There is little doubt that the interaction first introduced by Pippard in a discussion of ultrasonic attenuation and later used by him to predict the effect on the thermal conductivity,[8] accounts for the variation of the lattice conductivity with electronic mean free path. We may now hope to find out to what extent deviations from the theoretical predictions result from the simplifications inherent in the free-electron treatment and from the other simplifying assumptions.

[15] A. Conolly and K. Mendelssohn, Proc. Roy. Soc. (London) **A266**, 429 (1962).

[16] M. Garber, B. W. Scott, and F. J. Blatt, Phys. Rev. **130**, 2188 (1963); Phys. Rev. **136**, A729 (1964); M. H. Jericho, thesis, University of Cambridge, 1963 (unpublished); B. Dreyfus, A. Lacaze, P. Thomas, and L. Weil, J. Phys. Chem. Solids **24**, 219 (1963); see Ref. 1 for earlier references.

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Effect of Crystal Anisotropy on the Thermal Conductivity of Copper Alloys*

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The lattice thermal conductivity of copper alloys has been studied, taking account of the anisotropy of the crystal by using a modified Debye distribution having angular dependence. This is equivalent to replacing the elastic velocities (V_i) that occur in the usual Debye distribution by $V_i(\theta,\phi)$ and multiplying by $d\Omega/4\pi$. Lindenfeld and Pennebaker assumed an isotropic crystal and so used the usual Debye distribution in their calculation of the conductivity. Using the expressions for K_T and K_L (the contributions to the conductivity from the transverse and longitudinal modes) employed by Lindenfeld and Pennebaker and the elastic velocities found from elastic-constant data, the angular integration for the anisotropic average of the total conductivity was performed by using a Houston's average over the principal crystalline directions.

For $T/\rho_0>10^6$ (ρ_0 is the residual resistivity), the curves of the (conductivity)/$T\rho_0$ against T/ρ_0 are nearly linear, and in this region the largest departure between theory and experiment occur. These calculations give a slope which is approximately 5% lower than the Lindenfeld-Pennebaker theoretical result, while their result gave a slope which was about 650% higher than the experimental one. This indicates that the departure of the calculated conductivity from their experimental results cannot, at least for copper, be accounted for by anisotropy.

I. INTRODUCTION

RECENTLY, Lindenfeld and Pennebaker[1] have done numerical calculations for the thermal lattice conductivity of copper alloys (assuming an isotropic crystal) based on Pippard's[2] theory of the dependence of the electron-phonon interaction on the electronic mean free path. They found sizable differences between their experimental curve of $K/T\rho_0$ (K and T have their usual meaning and ρ_0 is the change in the residual resistivity) and their theoretical ones. They suggested, following Pippard, that this departure might be due to their neglect of anisotropy and the nonsphericity of the Fermi surface in copper. The former effect is considered in this paper.

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[1] P. Lindenfeld and W. B. Pennebaker, Phys. Rev. **127**, 1881 (1962).

[2] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).

II. CALCULATION OF THE CONDUCTIVITY

The expressions for the contributions of the transverse and longitudinal modes to the thermal conduc-