Thermal Conductivity of Dilute Indium-Mercury Alloys

A. M. Toxen, G. K. Chang, and R. E. Jones
International Business Machines Corporation, Thomas J. Watson Laboratory, Yorktown Heights, New York
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The thermal conductivities of a series of polycrystalline specimens of indium containing 0.1 to 2.5 at. % mercury have been measured in the temperature range 1.4°–4.0°K. By using an extrapolation procedure, the amount of phonon conduction in the superconductive state was calculated and was found to be about one-half as large as the value calculated from the theory of Bardeen, Rickayzen, and Tewordt. From the ratio of the electronic thermal conductivity in the superconductive state to that in the normal state, the temperature and composition dependences of the Bardeen-Cooper-Schrieffer (BCS) energy gap were calculated. Small systematic deviations of the measured gaps from the predictions of the BCS theory were observed.

INTRODUCTION

ALTHOUGH thermal conductivity measurements on superconductors may provide insight into the processes of superconductivity, the measurements are frequently difficult to interpret theoretically because several conductive and scattering mechanisms may be in operation simultaneously. In both the normal and superconductive states, heat transfer may occur via electrons and phonons. Hence, the total thermal conductivity will be the sum of the electronic and lattice contributions, i.e.,

$$K=K_e+K_g. \tag{1}$$

In metals which are not too impure, however, the thermal conduction is predominantly electronic and the scattering is by static imperfections and phonons. In this case, the electronic normal state conductivity at low temperatures is given to a first approximation by the theoretical expression

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

where A and B are constants.[1] To this approximation, B is independent of imperfection concentration, whereas A is proportional to the residual electrical resistivity ρ_0. Hence, one can infer from Eq. (2) that the electronic thermal resistivity is just the sum of two contributions: A/T, the resistivity caused by scattering by static imperfections; and BT^2, the intrinsic resistivity, i.e., the resistivity caused by phonon scattering. Actually, higher order calculations[2] indicate that B is not really independent of imperfection content, but increases with increasing residual resistivity. In the superconductive state, the situation is more complex. Near the critical temperature T_c, the main contribution to the thermal conduction is still electronic, except in very impure materials, and the scattering mechanisms operative are the same as those in the normal state. As the temperature decreases, however, the electronic conduction decreases while the lattice conduction increases until at about $0.2T_c$ the lattice conduction is dominant. Below about $0.1T_c$, the thermal conduction generally follows a T^3 law characteristic of boundary scattering of phonons.

The Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity[3] seems to be capable of predicting the relative values of the thermal conductivity in the normal and superconducting states provided that the conduction is by electrons and the scattering is due to static defects.[4] Conversely, thermal conductivity data can be used to check the variation of the BCS energy gap with temperature and purity. The chief difficulty in this procedure is in quantitatively determining that the thermal conduction is solely by electrons and the scattering is solely by static defects, or, in the cases where other scatterers or other conductors are present, to make the proper corrections.

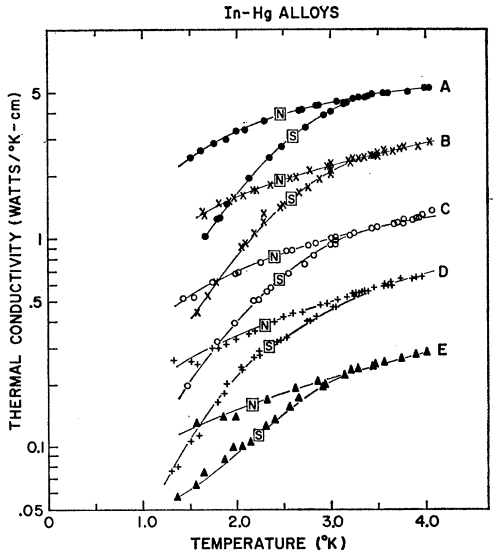

FIG. 1. The low-temperature thermal conductivity of indium-mercury alloys in the normal and superconducting states. Specimens *A*, *B*, *C*, *D*, and *E* contain, respectively, 0.1 at. % Hg, 0.2 at. % Hg, 0.5 at. % Hg, 1.0 at. % Hg, and 2.5 at. % Hg.

[1] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., p. 288.
[2] E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950).
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[4] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959), referred to hereafter as BRT.

TABLE I. Normal state properties of specimens.

Nominal composition (at. % Hg)	Constant A (deg^2 cm/watt)	Constant B (cm/watt deg)	$\alpha=BT_c^3/A$
pure[a]	0.034	1.11×10^{-3}	1.3
0.1	0.608	2.42×10^{-3}	0.157
0.2	1.247	3.15×10^{-3}	0.100
0.5	2.90	3.42×10^{-3}	0.046
1.0	5.90	...	~0
2.5	13.25	...	~0

[a] See reference 11.

In order to determine in this way the magnitude and temperature dependence of the BCS energy gap for indium, specimens containing from 0.1 to 2.5 at. % mercury have been measured. The results are shown in Fig. 1. It was found that at high reduced temperatures and low-impurity concentration it was necessary to correct for the scattering of electrons by phonons. This was done by using the expressions derived by Kadanoff and Martin[5] from a simple model for the combined effects of impurity and phonon scattering. At low temperatures and low purities a parallel conduction by phonons was found. This was corrected for by an extrapolation procedure.

The choice of indium-mercury alloys for this study was prompted by the fact that the metallurgy, critical temperatures, critical fields, and other superconducting properties had been investigated by Reeber.[6] The specimens used in this study were either specimens used in that study, or specimens prepared in a similar manner. The results of the preparation were polycrystalline extruded wires, known to be highly homogeneous.

THE NORMAL STATE

The normal-state thermal conductivity data could be fit to an expression: $1/K_n=A/T+BT^2$. This indicates that there was not a detectable amount of phonon conduction in the normal state for these specimens. The results for the alloy specimens are summarized in Table I.

The most exceptional feature of the data in Table I is the increase in the constant B, which is a measure of the phonon scattering of electrons, with increasing mercury content. According to the elementary theories of phonon scattering, this constant should depend only upon the Debye temperature and the "effective" number of free electrons present in the material under consideration. More refined calculations by Sondheimer[2] indicate a possible variation of B with mean free path of about 33%, but this is inadequate to explain the 300% variation shown in Table I.

The quantity α listed in Table I is equal to the ratio of the thermal resistance due to phonons to the resistance due to impurities, evaluated at the transition temperature. This constant is used in the model of Kadanoff and Martin to correct for the effects of phonon scattering in the superconducting state. For the alloys containing 1.0 and 2.5% mercury the magnitude of the term BT^2 was zero within the experimental uncertainty of the data. The value of α for these specimens was therefore less than about 0.02.

The thermal conductivity of the normal state at temperatures below the transition temperature is obtained by applying a sufficiently high longitudinal magnetic field to completely destroy superconductivity.

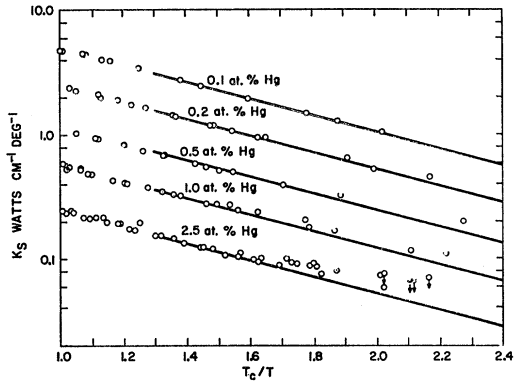

FIG. 2. The superconducting thermal conductivity as a function of T_c/T for specimens containing 0.1, 0.2, 0.5, 1.0, and 2.5 at. % Hg.

THE SUPERCONDUCTING STATE

In order to analyze the thermal conductivity in the superconducting state, it is necessary that the various mechanisms of heat conduction and scattering be identified. From the temperature dependence of the normal state conductivity, phonon scattering of electrons can be detected, and in this way discernible amounts were found in the specimens containing 0.1, 0.2, and 0.5 at. % mercury. It will be seen in the following analysis that phonon conduction in the superconducting state can be measured in the 0.5, 1.0, and 2.5 at. % mercury specimens.

In Fig. 2 the thermal conductivity in the superconducting state is plotted for all the specimens. In deducing the amount of phonon conduction, we take advantage of the fact that the plot of $\ln K$ vs (T_c/T) is approximately linear over the temperature range with which we are concerned, in the case of impurity scattering of electrons. (See Zavaritski.[7]) This can be seen from Fig. 3 in which is plotted $\log(tK_s/K_n)$ vs t^{-1}, where the K_s/K_n values are determined from the theoretical calculation of BRT and t is the reduced temperature T/T_c. The significance of this plot can be easily seen as follows. For the case of electronic thermal conduction with scattering by static imperfections, K_n is simply proportional to the absolute temperature

[5] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961).
[6] Morton D. Reeber, Phys. Rev. **117**, 1476 (1960).
[7] N. V. Zavaritskii, Soviet Phys.—JETP **10**, 1069 (1960).

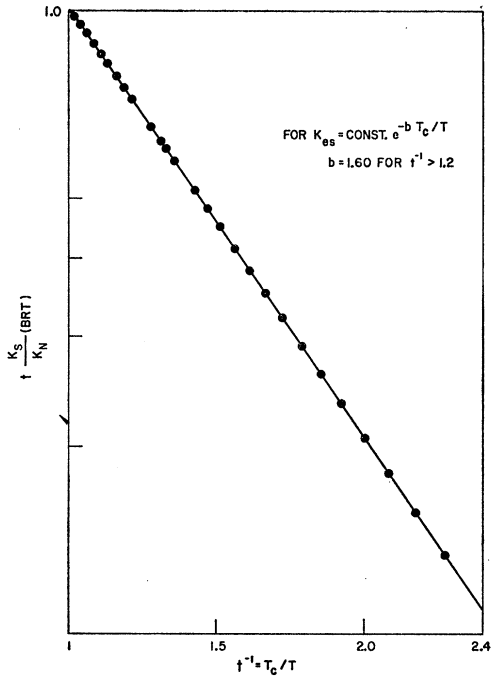

FIG. 3. The temperature variation of the electronic thermal conductivity which is predicted by the theoretical model of Bardeen, Rickayzen, and Tewordt.

[see Eq. (2)], or more precisely, K_n is equal to $tK(T_c)$, where $K(T_c)$ is the thermal conductivity at $T=T_c$. Hence, K_s is given by the expression

$$K_s=K(T_c)tK_s/K_n. \tag{3}$$

It can be seen from Fig. 2 that the purest specimens fit Eq. (3) quite well. In fact, it was possible on this plot to draw straight lines with the same slope through the data of all the specimens in the region $1.2<t^{-1}<1.5$ to within the experimental uncertainty. However, with the more impure specimens and higher values of T_c/T the conductivities fall above the extrapolation of this straight line. This "excess" conductivity we ascribe to phonon conduction.

The values for the lattice thermal conductivity which were obtained in this way can be compared to the predictions of Bardeen, Rickayzen, and Tewordt.[4] For our specimens there was no discernible lattice conduction in the normal state. Therefore, in order to compare with the results of BRT we used the values of lattice conductivity in the normal state inferred by Sladek[8] from his work with indium-thallium alloys. He found that the normal state lattice conductivity could be fit by the function $6\times10^{-4}\,T^2$ watt cm^{-1} deg^{-1} for very dilute specimens. Using this value and the BRT result, a quasi-theoretical curve for the lattice conductivity could be constructed and compared to the experimental values in Fig. 4.

[8] R. J. Sladek, Phys. Rev. **97**, 902 (1955).

The vertical bars in this plot correspond to an error of plus or minus 2% in the total superconducting conductivity from which the lattice conductivity was calculated. Even though the inaccuracy leaves something to be desired, it can be seen that the data agree with the theory in order of magnitude. However, a curve drawn at half the theoretical value gives a somewhat better fit to the experimental points. These results are also consistent with lattice conductivity measurements by other workers, such as Hulm,[9] Laredo,[10] and Sladek,[8] whose data indicate that the ratio of lattice conductivity in the superconducting state to that in the normal state is smaller than the ratio predicted by BRT.

Once corrections have been made for lattice conduction, there remains the task of accounting for the phonon scattering of electrons in the purest specimens near the transition temperature. The exact method of doing this remains one of the unsolved problems in superconductivity. The model of Kadanoff and Martin[5] predicts a decrease of the ratio of conductivities K_s/K_n where phonon scattering is appreciable; however, it fails to predict the correct ratios observed in very pure lead and mercury, and is in disagreement with the detailed calculations of BRT. On the other hand, the latter fails to predict the decrease in the K_s/K_n ratio in the presence of phonon scattering. We have, therefore, used the model of Kadanoff and Martin because it has been shown to be empirically successful in the cases of pure indium[11] and pure tin.[12] Further, it is hoped that the results are fairly insensitive to the exact nature of this correction since the phonon scattering is, in all of these specimens, known to be small.

The expression derived by Kadanoff and Martin is

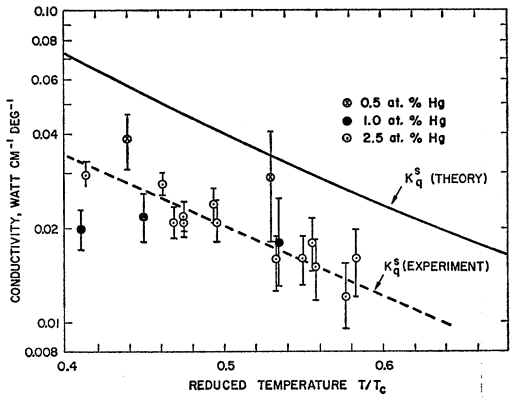

FIG. 4. The lattice thermal conductivity in the superconducting state vs T/T_c. The curve through the experimental points is one-half the theoretical curve.

[9] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).
[10] S. J. Laredo, Proc. Roy. Soc. (London) **A229**, 473 (1955).
[11] R. E. Jones and A. M. Toxen, Phys. Rev. **120**, 1167 (1960).
[12] A. M. Guénault, Proc. Roy. Soc. (London) **A262**, 420 (1961).

as follows:

$$\frac{K_s}{K_n}=3/2\pi^2\int_0^\infty d(\beta\epsilon)(\beta\epsilon)^2\,\mathrm{sech}^2\left(\frac{\beta E}{2}\right)$$
$$\times[1+\alpha(T/T_c)^3][\beta\epsilon/\beta E+\alpha(T/T_c)^3]^{-1}, \quad (4)$$

where the notation is that of BCS with the exception of the constant α, which is the ratio of the normal state electronic thermal resistance due to phonons at the transition temperature to that due to impurities. For the purposes of determining the BCS energy gap from this expression, it is sufficient to observe that once the ratio K_s/K_n, the reduced temperature T/T_c, and the ratio α are determined, the energy gap $\epsilon_0(t)$ is completely determined on the right-hand side of the expression.

THE ENERGY GAP

The results for the energy gap determined in this manner as a function of reduced temperature can be displayed in several ways. Perhaps the most natural is a plot of the energy gap itself as a function of the reduced temperature. An entirely equivalent plot is the ratio of the energy gap found from the thermal conductivity data to the value predicted by BCS. The smoothed energy-gap values calculated from the thermal conductivity data by means of Eq. (4) are shown in Fig. 5. For comparison, energy gaps were calculated using the BRT formula which does not take account of phonon scattering. These results are shown in Fig. 6. A comparison of Figs. 5 and 6 indicates that for temperatures below about $t=0.7$, the results are virtually identical, i.e., the phonon scattering is low enough that the calculated energy gap is insensitive to the model used to compute it. Hence, it is these results which are the most reliable. First, consider the lowest temperature $t=0.48$. From Fig. 5, it is clear

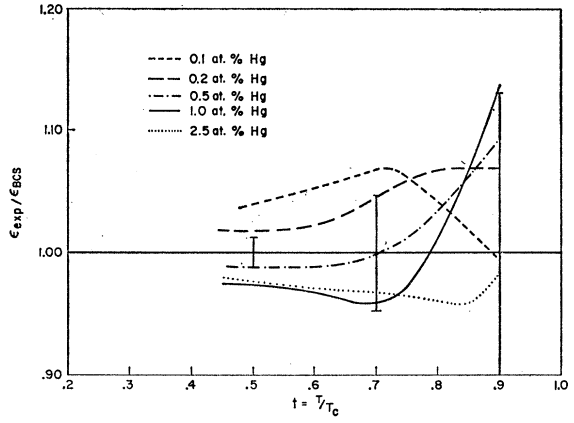

FIG. 5. The ratio of experimental energy gap to the theoretical BCS gap as calculated from the formula of Kadanoff and Martin.

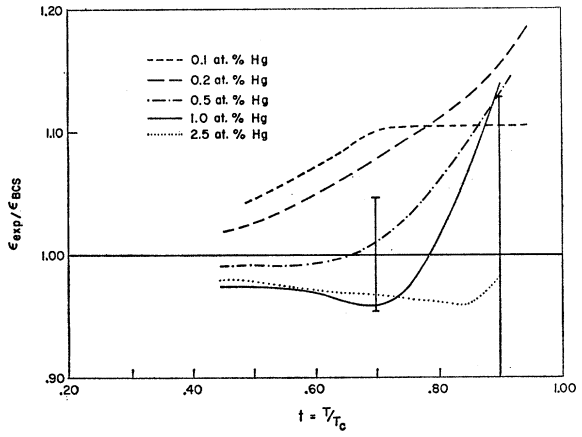

FIG. 6. The ratio of experimental energy gap to the theoretical BCS gap, as calculated from the model of Bardeen, Rickayzen, and Tewordt.

that the calculated energy gaps are in very good agreement with the weak coupling limit of the BCS theory; a variation of $\pm 4\%$ from the predicted values encompasses all five specimens. However, the magnitude of the deviation is composition dependent, i.e., it varies monotonically with critical temperature T_c. The specimen with the highest T_c, the 0.1 at. % Hg specimen with $T_c=3.402$°K, deviated by $+4\%$; the 0.98% specimen with the lowest T_c, 3.350°K, deviated by -2.6%. The temperature dependence of $\epsilon_{exp}/\epsilon_{BCS}$ is also dependent upon specimen composition. Again, consider the temperature interval $0.45<t<0.7$ in which the data are most reliable. For the most dilute alloy specimens, $\epsilon_{exp}/\epsilon_{BCS}$ increases with increasing temperature. It is significant that this type of deviation of the temperature dependence of the energy gap of indium from the prediction of BCS was also observed in ultrasonic attenuation experiments[13] as well as in tunneling experiments.[14] This behavior can be explained by the presence of an anisotropic energy gap such as that suggested by generalization of the microscopic theory of superconductivity[15] or deduced from ultrasonic attenuation experiments on tin single crystals.[16,17]

For the more concentrated alloys, the ratio $\epsilon_{exp}/\epsilon_{BCS}$ is more nearly temperature independent. This can be explained by assuming that the anisotropy of the gap is diminished as the mercury content is increased. This is just the result that would be expected from Anderson's theory of "dirty" superconductors.[18,19]

[13] R. W. Morse and H. V. Bohm, Phys. Rev. **108**, 1094 (1957).
[14] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[15] This concept was independently arrived at by several authors. See, for example, Leon N. Cooper, Phys. Rev. Letters **3**, 17 (1959).
[16] R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters **3**, 15 (1959).
[17] P. A. Bezuglyi, A. A. Galkin, and A. P. Korolynuk, Soviet Phys.—JETP **9**, 1388 (1959).
[18] P. W. Anderson, Bull. Am. Phys. Soc. **4**, 148 (1959).
[19] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).