

G. K. Chang
R. E. Jones
A. M. Toxen

Thermal Conductivity of Dilute Indium-Mercury Superconducting Alloys

Abstract: Thermal conductivities were measured for a series of polycrystalline alloys of indium containing 0.1 to 2.5 At.% mercury. Using theoretical models which relate the electronic thermal conductivity of a superconductor to its energy gap, the temperature and composition dependences of the energy gap have been calculated for these specimens. Estimates of the lattice thermal conduction were also obtained.

Introduction

The Bardeen, Cooper and Schrieffer theory of superconductivity¹ 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.² 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 to determine quantitatively that the thermal conduction occurs solely by electrons and the scattering is done solely by static defects or, in the cases where other scatterers or other conductors are present, to make the proper corrections to obtain the desired curves.

In order to determine in this way the temperature dependence of the BCS energy gap, indium specimens containing from 0.1 to 2.5 At.% mercury have been measured. It was found that at high reduced temperatures and higher purities it was necessary to correct for the scattering of electrons by phonons. This was done by using the expressions derived by Kadanoff and Martin³ 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 by an extrapolation procedure which employed the data of the higher purity specimens.

The choice of the indium-mercury alloys for this study was prompted by the fact that the metallurgy, critical temperatures, critical fields, and other superconducting properties had been thoroughly investigated by M. D. Reeber.⁴ The specimens used in this study were either specimens used in that study or specimens prepared in a similar manner and known to be highly

homogeneous. A description of the technique for measuring thermal conductivity can be found in a previous paper.⁵

Normal state

The normal state thermal conductivity data could be adequately represented by the 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. It also indicates that the resistance to electronic conduction could be ascribed to a term due to impurities, A/T , and a phonon term, BT^2 .

The results for the alloy specimens are summarized in Table 1. The most striking feature of these data 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. Judging from the behavior of other alloy systems, it is unlikely that these quantities vary by a sufficient amount to account for the observed changes in the constant B . Actually, higher order theoretical calculations⁶ indicate that B is not really independent of imperfection content, but increases with increasing residual resistivity. However, the observed increase in B is considerably greater than the increase predicted. A similar effect has been observed by A. M. Guénault⁷ in single-crystal indium and tin.

The quantity α listed in Table 1 is equal to the ratio of resistance due to phonons to the resistance due to impurities evaluated at the transition temperature.

This constant is used in correcting for the effects of phonon scattering in the superconducting state. For the alloys containing 1.0 and 2.5 percent mercury, the magnitude of the term BT^2 lies within the experimental uncertainty of the data. The value of α for these specimens was therefore less than about 0.02.

Superconducting state

In order that the decrease of the thermal conductivity that occurs during transition into the superconducting state be a test of the validity of the BCS theory, it is necessary to identify the various mechanisms of heat conduction and scattering. The normal-state data were used to determine the amount of phonon scattering, and discernible amounts were found in specimens containing 0.1, 0.2, and 0.5 At.% mercury. It will be seen in the following analysis that phonon conduction greater than the experimental uncertainty can be measured (in the superconducting state) in the 0.5, 1.0, and 2.5 At.% mercury specimens.

In Fig. 1 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 $\ln K^s$ vs (T_c/T) is linear in the case of impurity scattering of electrons in the range of (T_c/T) greater than about 1.2. It can be seen that this holds well for the purest specimens in this plot. In fact, it was possible on this plot to draw straight lines with the same slope (within the experimental uncertainty) through the data of all the specimens in the region $1.2 < T_c/T < 1.5$. However, with the more impure specimens and higher values of T_c/T the conductivities fall above this straight line. This excess conductivity we ascribe to phonon conduction.

The values of the lattice thermal conductivity which were obtained in this way can be compared to the predictions of Bardeen, Rickaysen, and Tewordt.² For our specimens there was no lattice conduction (in the normal state) which lay outside of experimental uncertainty. Therefore, in order to compare with the results of BRT, we used the values of lattice conductivity in the normal state inferred by Sladek⁸ from his work with concentrated indium-thallium alloys. By extrapolation of his results we find that the

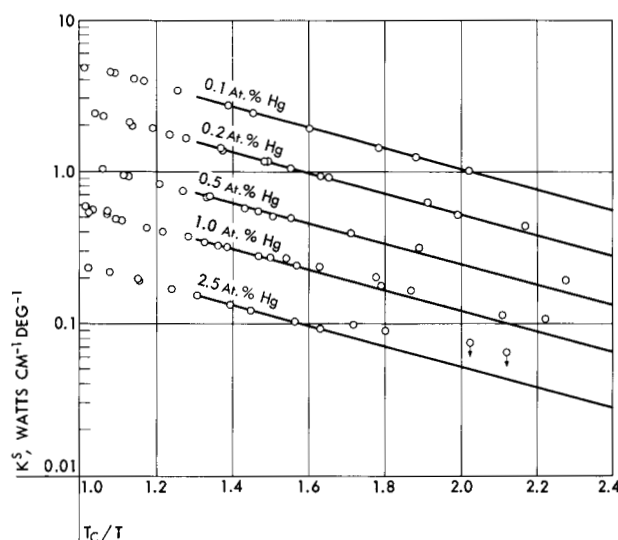


Figure 1 The superconducting thermal conductivity as a function of T_c/T for specimens containing 0.1, 0.2, 0.5, 1.0, and 2.5 At.% mercury.

normal-state lattice conductivity can be represented by the function $6 \times 10^{-4} T^2$ watt $\text{cm}^{-1} \text{deg}^{-1}$ for dilute specimens. Using this value and the BRT result, for the ratio of lattice conductivities a quasi-theoretical curve for the lattice conductivity in the superconducting state could be constructed and compared to the experimental values of Fig. 2.

The vertical bars in this plot correspond to an error of $\pm 2\%$ in the total superconducting conductivity from which the lattice conductivity was calculated. Even though the inaccuracy is great, 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. While the inaccuracy of this determination is probably too great to justify conclusions about the theory from these data alone, the data are consistent with the determinations of the lattice conductivities by other workers such as Hulm⁹ and Laredo,¹⁰ whose data

Table 1 Summary of results for In-Hg specimens

Nominal composition	Constant A	Constant B	$\alpha \equiv BT_c^3/A$
pure (see Ref. 5)	0.034 $\text{deg}^2 \text{cm/watt}$	$1.11 \times 10^{-3} \text{cm/watt deg}$	1.3
0.1 At.% Hg	0.608	2.4×10^{-3}	0.157
0.2	1.247	3.1×10^{-3}	0.100
0.5	2.90	3.4×10^{-3}	0.046
1.0	5.90	—	~ 0
2.5	13.25	—	~ 0

indicate that the ratio of superconducting lattice conductivity to normal-state lattice conductivity is less than the prediction of BRT.

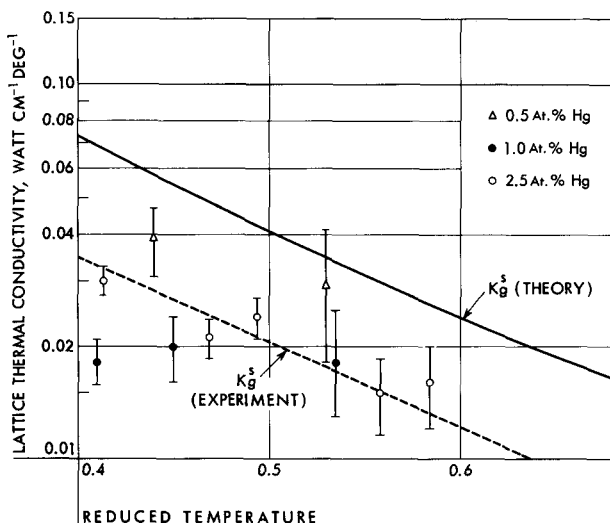
Once corrections have been made for lattice conduction, there remains the task of accounting for the phonon scattering of electrons in the purest specimens near the transition temperature. The development of the correct theory for this case remains one of the unfinished tasks for physicists concerned with the theory of superconductivity. The simple model of Kadanoff and Martin³ predicts a decrease of the ratio of conductivities, K^s/K^n , when phonon scattering is present; 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.¹¹ On the other hand, the detailed BRT theory fails to predict a decrease in the K^s/K^n ratio when phonon scattering occurs. We have, therefore, used the Kadanoff and Martin model because it has been shown to be empirically successful in the cases of pure indium⁵ and pure tin.⁷ Further, it can be hoped that the results are fairly insensitive to the exact nature of the correction since the phonon scattering is, in all of these specimens, known to be small.

The expression derived by Kadanoff and Martin is as follows:

$$K^s/K^n = \frac{3}{2}\pi^2 \int_0^\infty d(\beta\epsilon)(\beta\epsilon)^2 (\text{sech}^2 \beta E/2) \times [1 + \alpha(T/T_c)^3] \times [\beta\epsilon/\beta E + \alpha(T/T_c)^3]^{-1}, \quad (1)$$

where $E = (\epsilon^2 + \epsilon_0^2)^{1/2}$ and $\beta = 1/kT$, in the notation

Figure 2 The lattice thermal conductivity in the superconducting state versus T/T_c . The curve through the experimental points is one-half the theoretical curve.



of BCS; however, the constant α is the ratio of the normal-state electronic 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 temperatures T , T_c , and the ratio α are determined, the energy gap ϵ_0 is completely determined on the right-hand side of the expression.

The energy gap

The calculated values of the energy gap determined in this manner can be displayed (as a function of reduced temperature) 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 experimentally to the value predicted by BCS. It should be pointed out that this does not constitute an independent measurement of the energy gap, but is simply a method of displaying any deviations from the predicted temperature dependence of the BCS theory.

The smoothed data calculated in this way for the three specimens with observable phonon scattering are shown in Fig. 3. The vertical bars here represent deviations introduced by an estimated error of $\pm 2\%$ in K^s/K^n . The results show the experimentally derived energy gap is above the BCS value at the lower values of reduced temperature. While the over-all agreement with BCS is quite good (the experimental values are within 5% of the BCS value) the deviations do seem to lie outside the estimated experimental error. It seems unlikely that this deviation could be caused by any inadequacies of the Kadanoff and Martin model for combined phonon and impurity scattering. Even in the purest of these specimens, the amount of resistance in the normal state attributable to phonons does not exceed 3% of the total resistance in the region of reduced temperature below 0.6. This would indicate that the correction would be small regardless of the model used to make it, and, consequently, would be unlikely to change the result qualitatively.

At temperatures near the transition temperature, the experimentally derived energy gaps for the 0.1, 0.2, and 0.5 At.% mercury specimens also deviate from the BCS theory. However, the deviations from the theoretical result in this region lie within the experimental uncertainty, which is large near the transition temperature. Therefore, it is impossible to determine whether this feature is a reflection of the variation of the energy gap with increased impurity, experimental error, or an inadequacy in the Kadanoff and Martin model.

In Fig. 4, the smoothed curves are shown for the specimens which display phonon conduction in the superconducting state. In neither the 0.5 At.% nor the 1.0 At.% specimen was there a detectable amount of phonon scattering in the normal state. Therefore, once the data for these specimens are corrected for phonon conduction, the BRT expression for K^s/K^n in the

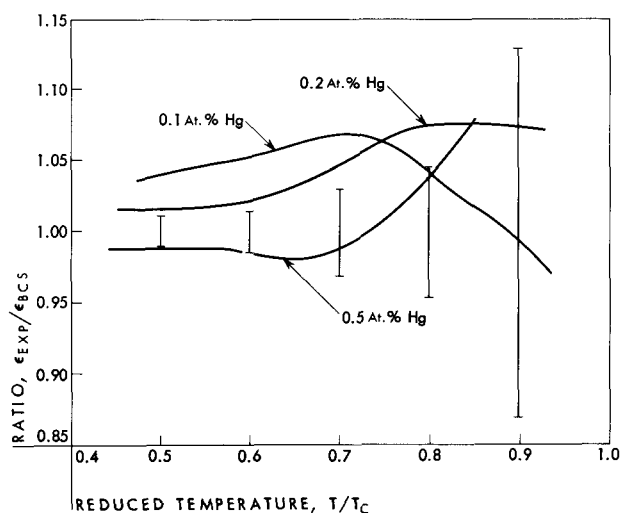


Figure 3 The ratio of experimental energy gap to the theoretical BCS gap for specimens with detectable phonon scattering.

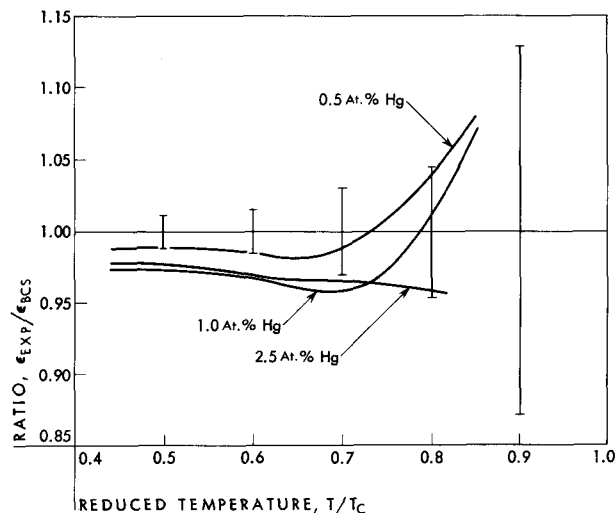


Figure 4 The ratio of experimental energy gap to the theoretical BCS gap for specimens with detectable phonon conduction.

presence of impurity scattering is applicable. Using the terminology of BCS this expression is:

$$K^s/K^n = \frac{3}{2}\pi^2 \int_{\epsilon_0}^{\infty} d(\beta E)(\beta E)^2 \operatorname{sech}^2 \beta E/2. \quad (2)$$

It is sufficient for present purposes to note that once K^s/K^n and the reduced temperature are specified, the energy gap is determined by the right-hand side of the expression.

Here again the data are generally in good agreement with the BCS prediction. The vertical bars again indicate the deviation caused by an uncertainty of $\pm 2\%$ in the K^s/K^n ratio. At higher values of reduced temperature, the curves lie within these limits of error. However, at lower reduced temperatures, the experimentally measured values of the energy gap lie below the theoretical values and outside the experimental error.

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