The group velocity v of the excitations is given by

$$v_s = (1/\hbar)\partial E/\partial k = (\epsilon_k/E_k)\cdot v_n .$$

For the mean free paths, one then has

$$l = v\tau = l_s = l_n .$$

Thus, if only elastic scattering is present, the two mean free paths must be equal. When inelastic phonon-scattering is present, a relaxation time cannot be defined unambiguously, and this simple discussion no longer applies.

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Reduction of the Lattice Thermal Conductivity of Superconductors due to Point Defects

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In the theory of the lattice thermal conductivity of solids the thermal resistivity can be regarded, as a first approximation, to be additively composed of the resistivity of the various scattering processes present. However, this approximation becomes progressively poorer, the more these scattering processes differ from each other in frequency dependence. In particular, in the lattice thermal conductivity of alloys, the scattering of phonons by electrons and by point defects (solute atoms) varies as the first and fourth power of frequency, respectively, and the additive resistance approximation underestimates the resistance. Furthermore, the effect of point defects is appreciable at somewhat lower temperatures than one would have expected from the additive resistance rule.

Hulm,[1] in his systematic analysis of the thermal conductivity of superconductors, makes use of the additive resistance approximation for the lattice thermal conductivity κ_g. Thus, he obtained the following relation for the normal state

$$1/\kappa_{gn} = W_e + W_p , \qquad (1)$$

and for the superconducting state

$$1/\kappa_{gs} = (W_e/h) + W_p , \qquad (2)$$

where W_e is the lattice thermal resistance due to phonon–electron scattering, W_p that due to all other scattering processes, and h, a function of T/T_c, is the reciprocal of the reduction of the phonon–electron scattering.

If W_p arises mainly from point defects, the additive resistance approximation is a poor one, and if one uses Eqs. (1) and (2) to determine the h function from observed values of κ_{gn} and κ_{gs}, this function should depend on the amount of point-defect scattering. Sladek[2] found, indeed, for a series of In–Tl alloys that the experimentally obtained h function varied with solute content.

Point defect scattering can have a pronounced effect on κ_{gs} even at low temperatures where W_p is negligible compared to W_e, because in the superconducting state W_e is reduced by $1/h$. Furthermore, this sensitivity will be increased if one discards the additive resistivity approximation [Eqs. (1) and (2)], but considers the effect of both scattering mechanisms on each phonon frequency separately.

A further complication arises when one considers that, in the treatment of the lattice thermal conductivity of superconductors[3] in terms of the BCS theory, this reduction of W_e arises from a reduction in the phonon scattering cross section, which is not by the same factor $1/h$ for all phonons, but which is significant only for phonons of energy $\hbar\omega$ less than the gap energy $2\Delta(T)$. The reason is that phonons with $\hbar\omega < 2\Delta(T)$ cannot decay into pairs of quasi-parti-

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[1] J. K. Hulm, Proc. Roy. Soc. (London) **A203**, 74 (1950).

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

[3] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959), referred to hereafter as BRT.

cles, but can only be scattered by those quasi-particles which, at a finite temperature, have been thermally excited. The latter contribution to the phonon decay rate, τ_{es}^{-1}, therefore decreases with temperature and vanishes at the absolute zero. The decay rate of phonons of $\hbar\omega > 2\Delta(T)$ is however virtually unaffected.

Thus, the increase in κ_{gs}/κ_{gn} will be small and insensitive to point defects for temperatures such that $2\Delta(T) < \hbar\omega_m \sim 3k_BT$, where ω_m is the frequency of the phonons which contribute maximally to κ_{gn}.

It is necessary to calculate the thermal conductivity by adding the effects of each scattering mechanism for each phonon frequency, and to integrate over all phonon frequencies. If one sets $\tau_{pn}^{-1} = A\omega^4$, $\tau_{en}^{-1} = B\omega$, and $\tau_{es}^{-1}/\tau_{en}^{-1} = g$, where τ_p and τ_e are the phonon lifetimes due to point defect and electron scattering, respectively, then the expression for κ_{gs}/κ_{gn} can be written as follows

$$\frac{\kappa_{gs}}{\kappa_{gn}} = \frac{\int_0^\infty dx\, x^3 e^x (e^x - 1)^{-2}[g(x) + \alpha t^3 x^3]^{-1}}{\int_0^\infty dx\, x^3 e^x (e^x - 1)^{-2}[1 + \alpha t^3 x^3]^{-1}} \qquad (3)$$

where $x = \hbar\omega/k_BT$, $t = T/T_c$, and α is given by

$$\alpha = (T_c/T_0)^3 = (k_BT_c/\hbar)^3(A/B)\,. \qquad (4)$$

The meaning of T_0 is that at the frequency $k_BT_0/\hbar$ the decay rates τ_{pn}^{-1} and τ_{en}^{-1} become equal. The function $g(x)$ has been given by BRT in terms of an integral expression, which depends on the temperature through the parameter $y = \Delta(T)/k_BT$.

If one calculates the strength of the point defect scattering from the mass-difference between solute and solvent atoms alone, then the constant A is determined by the formula[4]

$$A = (a^3/4\pi v^3)(\Delta M/M)^2 n\,, \qquad (5)$$

where a^3 is the volume per atom, v the velocity of sound, n the concentration (fraction per atom), M the mean atomic mass, and ΔM the deviation from M. It seems reasonable to neglect distortion effects for In–Tl and In–Hg alloys, in which we are mainly interested here, since the mass ratio is as high as 2:1. This procedure has been found satisfactory in other alloys of comparable mass ratio.[5]

The constant B can be expressed in terms of the experimental value for κ_{gn}/T^2, i.e.,

$$B = 7.2(2k_B^3/\hbar^2 v)\,(\kappa_{gn}/T^2)^{-1}\,. \qquad (6)$$

From Eqs. (2), (3), and (4), one obtains the following expression for α

$$\alpha = \frac{\pi^2 a^3}{7.2v^2\hbar}\left(\frac{\Delta M}{M}\right)^2\left(\frac{\kappa_{gn}}{T^2}\right) nT_c^3\,. \qquad (7)$$

For example, for indium containing 15% thallium α is about 3.2×10^{-3} and T_0 about 23°K. These values have been obtained by using for κ_{gn}/T^2 the experimental value of Sladek for very dilute In–Tl alloys, which is 6×10^{-4} W cm^{-1} deg^{-3}.

The integrals determining $g(x)$ for different values of x and y have been calculated numerically, since the analytic expression derived by BRT is valid only for $y > 2$, and since the integrals over x in Eq. (3) have to be evaluated numerically in any case. In Figs. 1 and 2 the universal curves for κ_{gs}/κ_{gn} versus

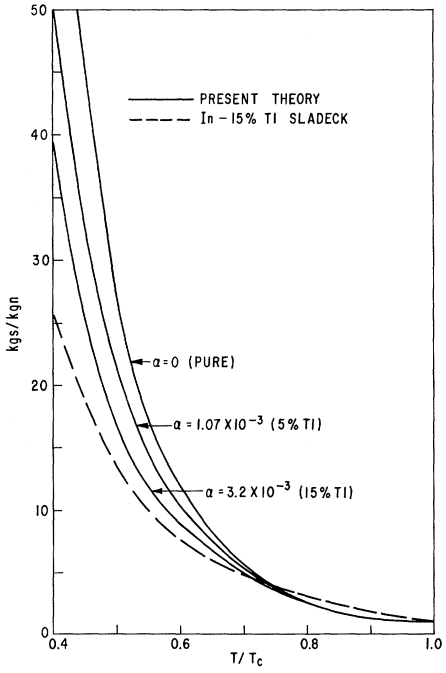

FIG. 1. Theoretical curves for the ratio of the lattice thermal conductivity in the superconducting state to that in the normal state, κ_{gs}/κ_{gn}, plotted versus T/T_c. The parameter α measures the scattering strength and concentration of the point defects. The corresponding Tl contents (in at. %) for In–Tl alloys are shown in brackets. The broken line is Sladek's experimental curve for indium containing 15% thallium.

$t = T/T_c$ are shown for a number of parameter values α. These values of α correspond to In–Tl alloys with thallium contents ranging from 2.5 to 30 at. %. In transforming from $y = \Delta(T)/k_BT$ to t we have assumed that $\Delta(T)/\Delta(0)$ as a function of t is given by the BCS curve, and further, that the ratio $2\Delta(0)/k_BT_c$ is equal to the BCS value 3.5. The $(\kappa_{gs}/\kappa_{gn})$ curve for the pure metal ($\alpha = 0$) lies below the curve shown

[4] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[5] P. G. Klemens, G. K. White, and R. J. Tainsh, Phil. Mag. **7**, 1323 (1962).

by BRT for values of $t > 0.7$ and has a zero slope at $t = 1$. One recognizes that the reduction of κ_{gs}/κ_{gn} due to point defect scattering becomes appreciable for $t < 0.7$, or $2\Delta(T) > 4k_BT$, and that it increases rapidly with decreasing t. The results for $t < 0.4$ have

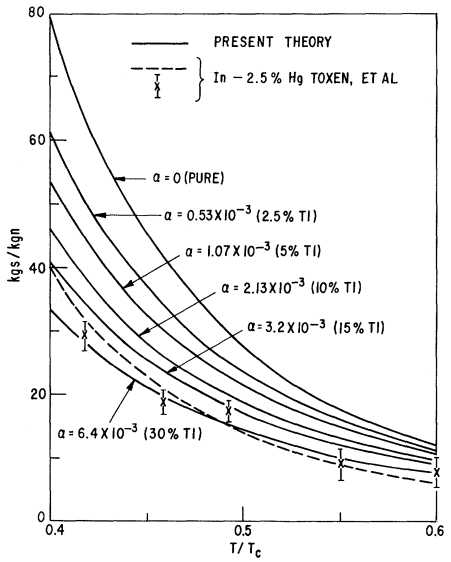

FIG. 2. κ_{gs}/κ_{gn} versus T/T_c for different α. The broken line is the curve which has been drawn by Toxen, Chang, and Jones, to fit their data on indium containing 2.5% mercury.

been omitted since at the lower temperatures other phonon scattering mechanisms, such as grain boundary or dislocation scattering, become predominant.

For comparison we have included in Fig. 1 Sladek's[2] experimental curve for In-15% thallium, and in Fig. 2 the points for In-2.5% mercury of Toxen, Chang, and Jones.[6] The two alloys have practically the same mass ratio. Also shown in Fig. 2 is a curve drawn at half the BRT curve, used by the latter authors as a fit to their results. One can see that the discrepancy between theory and experiment has been substantially reduced by the point defect scattering, but by no means eliminated.

In the case of In-15% thallium the remaining discrepancy, which is largest at lowest temperatures, could be due to some other imperfection. For example, a dislocation resistance, about 2% of W_e in magnitude, would account for this discrepancy. This would correspond to a dislocation density of the order of 10^9 per cm^2. Such values are not uncommon in alloys.[7]

In the case of In-2.5% mercury the discrepancy is considerably larger. However one should remember that κ_{gn} was not measured directly in this case, but inferred from Sladek's results on In–Tl. In this alloy the value of κ_{gn} may well be different, particularly in view of the rapid increase of the ideal electronic thermal resistance with mercury content.[6] This would, of course, falsify the experimental $(\kappa_{gs}/\kappa_{gn})$ values. Another possibility is that the neglect of distortion effects in calculating the phonon scattering cross section may not be justified for mercury in indium. It is suggestive that mercury in indium changes the tetragonal distortion ratio c/a about three times as much as does thallium in indium.[8]

The authors would like to express their gratitude to J. Prewitt for providing the program for the numerical calculations, which have been carried out at the Bell Laboratories.

[6] A. M. Toxen, G. K. Chang, and R. E. Jones, Phys. Rev. **126**, 919 (1962).

[7] W. R. G. Kemp and P. G. Klemens, Australian J.Phys. **13**, 247 (1960).

[8] See, for example, M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

Discussion 16

J. L. OLSEN, *Zurich*: Could Tewordt explain why his work on lead and mercury leads to a series of curves? This would be in agreement with the experimental results for these metals in contradistinction to the situation in indium where there's apparently a single curve.

L. TEWORDT, *University of Notre Dame:* For weak coupling superconductors, one gets a universal curve at reduced temperature. For lead and mercury, one has to solve the gap integral equation which contains the coupling constant and the Debye temperature, so that one obtains not a universal curve, but material-dependent ones.