expression for the Hall coefficient

$$R=\frac{R_1\sigma_1^2+R_2\sigma_2^2}{(\sigma_1+\sigma_2)^2}, \tag{1}$$

depends on the Hall coefficients R_1, R_2 and conductivities σ_1, σ_2 of the two bands, and therefore has too many unknown quantities for a quantitative comparison with experiment. However it does allow for the presence of either sign of Hall coefficient depending upon whether electron or hole conduction predominates in the sense of Eq. (1), and is useful for a qualitative interpretation of the results. The Hall coefficient in pure tin is very small and negative at room temperature. This would indicate not a large number of conduction electrons but rather a delicate balance between electron and hole conduction. The fact that at 75°K the Hall coefficient is positive indicates that the temperature dependence of the conductivities in the two bands is sufficiently different to swing the balance in favor of hole conduction at the lower temperature. However, even a small percentage of bismuth added, corresponding to an increase of the electron-atom ratio, is sufficient to reverse the sign of the Hall coefficient. The Hall coefficient, however, reverses sign again at about 8 at. % bismuth, reaches a peak positive value at 10 at. % bismuth, and is rapidly dropping toward negative values again at the highest atomic percent bismuth sample studied. On the basis of the density of states curve shown one would not expect quite the same behavior. The sharp drop in density of states between 4 and 6 at. % bismuth, and the rising portion beyond 6 at. % indicate that complete filling of the lower band is taking place around 6 at. % bismuth, beyond which electron conduction predominates. Because of the behavior of the Hall coefficient one can only conclude that the lower band (holes) does not drop sharply to zero just beyond 6 at. % as the extrapolation of the density of states indicates, but rather tails off in such a way that holes are present even out to 12 at. % bismuth. Their density however must be small, and since the Hall coefficient is positive in the presence of higher density of electrons in the upper band, one can only conclude that the holes have a much higher mobility than the electrons. Upon complete filling of the lower band the Hall coefficient must become negative again, and it is gratifying to note a strong tendency in this direction beyond 10 at. % bismuth.

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Thermal Resistance due to Point Defects at High Temperatures

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An expression is obtained for the lattice thermal conductivity at high temperatures in the limit when the scattering of phonons by point defects is stronger than by umklapp processes. The latter limit the phonon mean free path at low frequencies and most of the heat is transported at frequencies such that the point defect and umklapp mean free paths are equal. The conductivity varies as $(AT)^{-\frac{1}{2}}$, where A is proportional to the strength of the point defect scattering, T is the temperature. The theory is in rough agreement with the thermal conductivity of Ge-Si alloys, measured by Steele and Rosi.

I. INTRODUCTION

THE lattice thermal conductivity is given by

$$\kappa=\frac{1}{3}\int S(\omega)v^2\tau(\omega)d\omega, \tag{1}$$

where $S(\omega)d\omega$ is the specific heat per unit volume due to lattice modes of frequency ω, $d\omega$, v is the velocity of the lattice waves, and $\tau(\omega)$ their effective relaxation time. If the phonons are scattered by various interaction processes, each process contributes additively to $1/\tau$, except that anharmonic three-phonon processes which conserve the total wave vector (N processes) do not contribute directly to the thermal resistance, but require special consideration.[1]

Point defects scatter phonons and contribute to the inverse relaxation time as

$$1/\tau'=A\omega^4. \tag{2}$$

They thus increase the thermal resistance. In the present paper we shall discuss their effect on the thermal resistance at temperatures at and above the Debye temperature θ in the limit when the point defect resistance is larger than the intrinsic resistance. Previous authors[1–3] have discussed the low-temperature point defect resistance in terms of τ', but relatively little attention has been paid to the high-temperature case; Ambegaokar[4] has, however, considered the high-temperature point

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[2] J. M. Ziman, Can. J. Phys. **34**, 1256 (1956).

[3] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[4] V. Ambegaokar, Phys. Rev. **114**, 488 (1959).

defect resistance in the case when it is much smaller than the intrinsic resistance.

The magnitude of the point defect scattering has been discussed by Klemens,[5] who obtained expressions for $1/\tau'$ due to the mass difference of the defect, differences in the binding between the defect and its neighbors, and anharmonic effects of the distortion about the defect. Of these quantities, the only one which is usually well known is the mass difference; furthermore the theory of mass defect scattering involves fewer approximations than the theory of distortion and misfit scattering. The theory may thus be tested quantitatively in the case of an alloy of atoms of widely different mass, such as Ge-Si. The thermal conductivity of some Ge-Si alloys has been measured at 80°K and 300°K by Steele and Rosi.[6]

II. THEORY

The intrinsic resistance at high temperatures is due to anharmonic three-phonon processes which do not conserve the total wavevector (U processes). Their inverse relaxation time at $T \overset{\sim}{>} \theta$ is of the form[1,7]

$$1/\tau_u = B\omega^2 \tag{3}$$

where $B \propto T$. This expression applies to frequencies not too close to the Debye limit.

If point defects scatter mainly in virtue of their mass difference, the scattering is described by a relaxation time (2) with

$$A = (a^3/4\pi v^3)\epsilon \tag{4}$$

where a^3 is the atomic volume, v the phonon velocity, and

$$\epsilon = \sum_i c_i (M_i - M)^2/M^2 \tag{5}$$

$$M = \sum_i c_i M_i \tag{6}$$

and where c_i and M_i is the concentration and mass of atoms of type i.

With U processes and point defect scattering acting together,

$$\tau(\omega) = \tau'\tau_u/(\tau' + \tau_u). \tag{7}$$

This equation disregards the effects of N processes. While these processes do not directly cause thermal resistance, they tend to make $\tau(\omega)$ independent of ω, and thus enhance the effectiveness of the other scattering processes, particularly of those whose relaxation time varies strongly with frequency.[7] However N processes and U processes occur with comparable frequency at high temperatures and if at high frequencies $\tau' < \tau_u$, then the effect of N processes on $\tau(\omega)$ will be small at these frequencies. At low frequencies, on the other hand, where $\tau' > \tau_u$, $\tau(\omega)$ is determined principally by $\tau_u(\omega)$, and since $\tau_u(\omega)$ does not vary too rapidly with frequency, the effect of N processes will not be too severe.[7] We are therefore justified in disregarding N processes in the present case of strong point defect scattering.

Substituting (7) into (1) and using for $S(\omega)$ the high-temperature limit

$$S(\omega) = \frac{3K}{2\pi^2}\frac{\omega^2}{v^3}, \tag{8}$$

where K is the Boltzmann constant,

$$\kappa = \frac{K}{2\pi^2 v}\int_0^{\omega_D} \omega^2 \frac{\tau'\tau_u}{\tau' + \tau_u} d\omega. \tag{9}$$

Ambegaokar[4] has used (9) in the limit of weak point defect resistance ($\tau' > \tau_u$ for all ω). In general (9) becomes

$$\kappa = \frac{K}{2\pi^2 v B}\int_0^{\omega_D} \frac{d\omega}{1 + \omega^2 A/B}. \tag{10}$$

One can define a frequency ω_0 by

$$\tau_u(\omega_0) = \tau'(\omega_0) \tag{11}$$

so that

$$\kappa = \frac{K}{2\pi^2 v}\frac{\omega_0}{B}\tan^{-1}\frac{\omega_D}{\omega_0}. \tag{12}$$

The thermal conductivity in the absence of point defects is, from (3),

$$\kappa_0(T) = \frac{K}{2\pi^2 v}\frac{\omega_D}{B} \tag{13}$$

so that κ of (12) can be expressed in terms of κ_0.

We are interested in the extreme case of strong point defect scattering, when $\tau'(\omega_D) \ll \tau_u(\omega_D)$, i.e., when $\omega_0 \ll \omega_D$. In that case $\tan^{-1}(\omega_D/\omega_0) = \pi/2$, and

$$\kappa = \frac{\pi}{2}\kappa_0 \frac{\omega_0}{\omega_D}. \tag{14}$$

From (11)

$$\omega_0 = (B/A)^{\frac{1}{2}} \propto T^{\frac{1}{2}}\epsilon^{-\frac{1}{2}} \tag{15}$$

and since $B \propto T$, and since $\kappa_0 \propto T^{-1}$,

$$\kappa \propto T^{-\frac{1}{2}}\epsilon^{-\frac{1}{2}} \tag{16}$$

in contrast to the case of weak point defect scattering,[4] when the additional thermal resistivity is independent of T and proportional to ϵ.

It should be noted that because $\tau'(\omega)$ decreases so rapidly with increasing ω, most of the heat is carried by the modes of frequency ω_0, in contrast to the case of intrinsic conduction, where most of the heat is carried by the modes of highest frequency ω_D. Thus (12) is relatively insensitive to deviations of the frequency spectrum from the Debye model. Even more significant is the fact that (12) and (14) are insensitive to any deviations of τ' from (2) at highest frequencies. Such deviations must occur whenever scattering is strong.

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

[6] M. C. Steele and F. D. Rosi, J. Appl. Phys. **29**, 1517 (1958).

[7] P. G. Klemens in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

TABLE I. Thermal resistivity W of germanium-silicon alloys.

Composition atomic % Si	ϵ	$W(80)$	$W(300)$ (cm-deg-watt^{-1})	$W_0(300)$	$(W/W_0)_{300}$	$(2\omega_D/\pi\omega_0)_{300}$	$W(300)/W(80)$
0	0.00	0.3	1.7	1.7	...	...	$\sim$6
11	0.04	2.8	4.9	1.6	3.1	2.2	1.8
35	0.14	3.9	7.8	1.3	6.0	4.1	2.0
56	0.22	4.7	9.3	1.1	8.5	5.2	2.0
90	0.15	2.3	5.3	0.8	6.6	4.3	2.3
100	0.00	0.1	0.7	0.7	...	...	$\sim$7
						Present theory	1.9

For example, if $\epsilon \sim 1$, expression (4) leads to a mean free path at highest frequencies which is less than a lattice spacing; clearly perturbation theory fails in this case and grossly overestimates the scattering. Nevertheless we can still expect the present theory to give a reasonable result for this case of strong scattering.

Because most heat is carried by relatively low frequencies, we would expect (12) and (16) to hold also for temperatures somewhat below θ.

III. APPLICATION TO Ge-Si ALLOYS

Steele and Rosi[6] have measured the thermal conductivity of germanium, silicon, and Ge-Si alloys containing 11, 35, 56, and 90% Si at 80° and 300°K. These alloys meet the condition that the point defect resistance is much larger than the intrinsic resistance. Furthermore, it is highly probable that the impurity atoms scatter mainly because of their mass difference, since germanium and silicon are chemically similar and since their lattice spacing differs only by a small amount.

To test (14) quantitatively, note that

$$\frac{\omega_0}{\omega_D}=\left[\frac{Kv}{a^3 q_D \epsilon \kappa_0}\right]^{\frac{1}{2}} \tag{17}$$

where $q_D=\omega_D/v$ is the Debye limiting wave number, κ_0 is the intrinsic thermal conductivity. For intermediate compositions neither v nor κ_0 are well known. However, according to a relation by Leibfried and Schloemann,[8] $\kappa_0 \propto Mv^3$ and $v \propto M^{-\frac{1}{2}}$. Thus if the difference in the properties of germanium and silicon were to arise solely from their mass-difference, v/κ_0 would vary as $M^{-\frac{1}{2}}$ and ω_0/ω_D should be practically independent of composition, except for the factor $\epsilon^{-\frac{1}{2}}$.

Thus using values of v and a for germanium, and using the observed value of $\kappa_0 T = 1.5\times10^2$ watt-cm^{-1}, we obtain

$$\omega_0/\omega_D = 3.3\times10^{-3}(T/\epsilon)^{\frac{1}{2}}$$

where T is expressed in °K.

In Table I values of $2\omega_D/\pi\omega_0$ at 300°K, calculated from (18), are compared with observed value of $W/W_0 = \kappa_0/\kappa$ at 300°K for various Ge-Si alloys.[6] Values of W_0 for the various alloys were estimated from the observed values of the two elements by linear interpolation. It will be seen that the present theory consistently overestimates κ/κ_0 by a factor ~ 1.5; however within a range of ϵ over a factor 5 the $\epsilon^{\frac{1}{2}}$ variation of W seems to be satisfied. Even for the 11% alloy $W=3W_0$ and $\omega_D/\omega_0 = 3.4$, hence the basic assumption that $\tau_u(\omega_D) \gg \tau'(\omega_D)$ seems satisfied for this and for all other cases.

The temperature dependence of $W \propto T^{\frac{1}{2}}$ seems also to be roughly satisfied for all these alloys between 80° and 300°K, even though one would expect the theory to break down at lower temperatures, especially for low values of ϵ. The value of $W(80)$ for the 11% alloy is certainly already somewhat high.

The reason for the discrepancy from (14) by a factor of about 1.5 lies probably in a failure of (13) relating B and κ_0. The expression for κ_0 is fairly sensitive to the behavior of the lattice waves near the zone boundary, and it is known that the dispersion of the lattice waves is particularly strong in germanium and silicon. A discrepancy of the present magnitude is thus not too unreasonable.

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