Low-Temperature Lattice Thermal Conductivity

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(Received December 13, 1960)

The effect of point imperfections on lattice thermal conductivity is discussed with particular attention to the case in which the temperature is low but the normal three-phonon scattering is still dominant. The experimental results of Walker and Fairbank on the conductivity of isotopic mixtures of solid helium are analyzed.

INTRODUCTION

IN previous work, a simple, phenomenological model for the calculation of lattice thermal conductivity was proposed and applied to the study of the conductivity of germanium at low temperatures.[1] The assumptions of this theory were: (1) All phonon-phonon scattering processes can be represented by relaxation times which are functions of the wave vector of one mode only. (2) The phonon distribution is characterized by a Debye spectrum. Effects due to anisotropy and dispersion are neglected. (3) The additivity of reciprocal relaxation times for independent scattering processes is assumed. A correction has to be made to allow for the special character of normal three-phonon scattering processes. These processes, which conserve the sum of the wave vectors of the phonons, can not by themselves produce a thermal resistance.

On the basis of these considerations, the following expression was obtained for the thermal conductivity, κ, [Eqs. (16), (19)–(21) of reference 1]:

$$\kappa = \frac{K}{2\pi^2 v_s}\left(\frac{KT}{\hbar}\right)^3 \left\{ \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x-1)^2}dx \right.$$
$$\left. + \left[\int_0^{\theta/T} \frac{\tau_c}{\tau_N}\frac{x^4 e^x}{(e^x-1)^2}dx\right]^2 \middle/ \right.$$
$$\left. \int_0^{\theta/T} \frac{1}{\tau_N}\left(1-\frac{\tau_c}{\tau_N}\right)\frac{x^4 e^x}{(e^x-1)^2}dx \right\}. \quad (1)$$

In this equation, K is Boltzmann's constant, v_s is the velocity of sound, θ is the Debye temperature, and x is the usual dimensionless variable $\hbar\omega/KT$. The relaxation times appearing in Eq. (1) are the following: τ_N is the relaxation time for the normal three-phonon scattering processes mentioned above; τ_c is a combined relaxation time, whose reciprocal is the sum of the reciprocal relaxation times for all the scattering processes. If, for instance, in addition to the normal three-phonon scatterings, we consider Umklapp processes, scattering by point defects, and boundary scattering (relaxation times τ_u, τ_D, and τ_B, respectively), then

$$\tau_c^{-1} = \tau_N^{-1} + \tau_u^{-1} + \tau_D^{-1} + \tau_B^{-1}. \quad (2)$$

The thermal conductivity as given by (1) becomes

infinite in the limit in which τ_c approaches τ_N, as is required by general considerations.

In a subsequent report, the contribution of point imperfections to the thermal resistivity was studied in detail,[2] and the results were applied to an analysis of the data of Berman *et al.* on the effect of varying the relative concentration of the isotopes Li[6] and Li[7] on the thermal conductivity of lithium fluoride.[3] The discussions of that paper were, for the most part, concerned with situations in which the approximation of the additivity of reciprocal relaxation times is valid. This occurs at high temperatures, or at low temperatures if either the point defect scattering or the Umklapp scattering is large. (Precise criteria will be developed below.) Under these conditions, the second term in (1) may be neglected.

The relaxation time for Umklapp processes should exhibit an exponential temperature dependence at low temperatures[4] ($\tau_u \propto e^{\theta/aT}$). Consequently, the contribution of the Umklapp processes to the thermal resistivity decreases very rapidly with decreasing temperature. In pure, single-isotope material, the situation may then be attained in which the addition of reciprocal relaxation times is not valid, and the second term of (1) dominates the conductivity. Such a situation was apparently achieved in the experiments of Walker and Fairbank on the thermal conductivity of isotopic mixtures of solid helium.[5,6] Under these circumstances, the thermal resistance shows a dependence on the residual isotopic disorder or defect content which is abnormally strong compared to that obtained when the additivity of reciprocal relaxation times is justified. This result was first predicted by Ziman[7]; it was observed in reference 2 that Ziman's result is a consequence of Eq. (1).

The object of this work is to study the effect of point imperfections on the thermal conductivity in detail for circumstances in which the second term of Eq. (1) must not be neglected. The data of Walker and Fairbank will then be analyzed with the object of showing that the

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

[2] J. Callaway and H. C. von Baeyer, Phys. Rev. 120, 1149 (1960). This paper is referred to as I.
[3] R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) A253, 403 (1959).
[4] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), Chap. 2.
[5] E. J. Walker and H. A. Fairbank, Phys. Rev. 118, 913 (1960).
[6] F. W. Sheard and J. M. Ziman, Phys. Rev. Letters 5, 139 (1960).
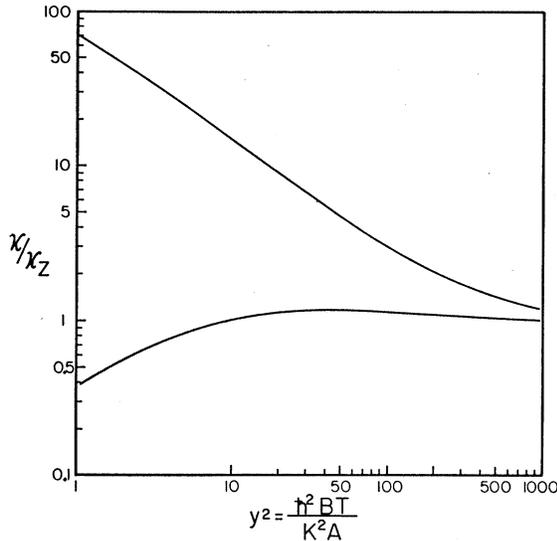[7] J. M. Ziman, Can. J. Phys. 34, 1256 (1956).

FIG. 1. The ratio of the conductivity of material containing point defects to the conductivity in the Ziman limit is given as a function of the variable: $y^2 = \hbar^2 B_N T / K^2 A$. The upper curve shows the total conductivity; the lower curve is the normal process correction discussed in the text.

simple theory is capable of giving a reasonable account of the experimental results, without requiring arbitrary assumptions as to the distribution of the isotopes.

CALCULATION OF THE THERMAL RESISTIVITY

Let us consider first a case in which Umklapp and boundary scatterings may be neglected, so that the only scattering processes to be considered are defect scattering and normal three-phonon scatterings. Then $\tau_c^{-1} = \tau_D^{-1} + \tau_N^{-1}$. If $\tau_D \gg \tau_N$ for frequencies of the order $KT/\hbar$, we may make an asymptotic expansion of the integrands in Eq. (1). The leading term in the expression for the resistivity $(W = \kappa^{-1})$ is

$$W = \frac{2\pi^2 v_s}{\hbar}\left(\frac{\hbar}{KT}\right)^3 \int_0^{\theta/T} \frac{1}{\tau_D}\frac{x^4 e^x}{(e^x-1)^2}dx \Bigg/$$

$$\left[\int_0^{\theta/T} \frac{x^4 e^x}{(e^x-1)^2}dx\right]^2. \quad (3)$$

This is essentially the formula derived by Ziman[7] from a variational principle. It has also been found independently by Tavernier.[8] According to Klemens,[9] the relaxation time for scattering by point defects is inversely proportional to the fourth power of the frequency:

$$\tau_D^{-1} = A\omega^4 = A(KT/\hbar)^4 x^4. \quad (4)$$

Klemens has also given an approximate expression for estimation of the proportionality constant, A. At very

[8] J. Tavernier, Ph.D. thesis, University of Paris, 1960 (unpublished).
[9] P. G. Klemens, Proc. Phys. Soc. (London) A68, 1113 (1955).

low temperatures, the upper limit of the integrals in (3) may be made infinite. Then

$$W = W_Z = 120\pi^2 v_s A T/\hbar. \quad (5)$$

In this limit, the defect resistance is twenty-five times greater than that predicted for the situation in which Umklapp processes dominate the phonon scattering [Eq. (16) of reference 2]. Equation (5) must be regarded as pertaining to an idealized limiting case (which will be called the Ziman limit) and should be an upper bound to the defect resistance.

To extend the calculation, it is necessary to make some assumptions concerning the form of the relaxation time for the normal three-phonon scattering processes. As in I, we set

$$\tau_N = B_N T^3 \omega^2. \quad (6)$$

We then define the variable y^2 as the ratio of the relaxation times τ_D/τ_N at a frequency $KT/\hbar$:

$$y^2 = \hbar^2 B_N T/K^2 A. \quad (7)$$

It is then possible to express the thermal conductivity simply in terms of certain integrals of the form:

$$\mathcal{J}_n(y,\theta/T) = \int_0^{\theta/T} \frac{x^{2n}}{x^2+y^2}\frac{e^x}{(e^x-1)^2}dx. \quad (8)$$

If we define $\kappa_Z = W_Z^{-1}$, where W_Z is given by (5), we find after some algebra that

$$\frac{\kappa}{\kappa_Z} = 60\left\{\mathcal{J}_1(y,\theta/T) + y^2\frac{\mathcal{J}_2^2(y,\theta/T)}{\mathcal{J}_4(y,\theta/T)}\right\}. \quad (9)$$

The first term of (9) is equivalent to the thermal conductivity as calculated in I, the second term represents the normal process "correction" which leads to the Ziman limit as $y^2 \to \infty$.

In order to simplify the evaluation of the integrals in (9) and in the subsequent discussion, we consider only temperatures sufficiently low so that the upper limit θ/T may be made infinite. We shall refer to the limit of $\mathcal{J}_n(y,\theta/T)$ as $\theta/T \to \infty$ as $\mathcal{J}_n(y)$. The necessary computations are greatly simplified by a recurrence relation which is a consequence of the substitution of the simple algebraic identity,

$$x^2(x^2+y^2)^{-1} = 1 - y^2(x^2+y^2)^{-1}$$

into (8):

$$\mathcal{J}_n(y) = \mathcal{J}_n(0) - y^2\mathcal{J}_{n-1}(y). \quad (10)$$

The quantities $\mathcal{J}_n(0)$ are standard definite integrals. We have

$$\mathcal{J}_n(0) = (2n-2)!\zeta(2n-2),$$

where ζ represents the Riemann zeta function.

The result of the evaluation of Eq. (9) is exhibited in Fig. 1. The upper curve represents the entire conductivity as given by (9); the lower curve shows the contribution from the second term of (9). It is seen that the

normal process correction is less than 10% of the conductivity for $y^2 < 15$; for y^2 as large as 100, it amounts to only one-third of the conductivity. Consequently, the results given in I, in which this correction was largely ignored, have a substantial range of validity. The additivity of reciprocal relaxation times would appear to be a very useful approximation in many circumstances.

Let us now consider the effect of inclusion of Umklapp and boundary scattering. In the limit that the relaxation times for these processes are much longer than τ_N, we obtain, instead of (3)

$$W = \frac{2\pi^2 v_s}{K}\left(\frac{\hbar}{KT}\right)^3 \int_0^{\theta/T}\left[\frac{1}{\tau_D}+\frac{1}{\tau_u}+\frac{1}{\tau_B}\right]\frac{x^4 e^x}{(e^x-1)^2}dx \Big/ \left[\int_0^{\theta/T}\frac{x^4 e^x}{(e^x-1)^2}dx\right]^2. \quad (11)$$

An expression equivalent to this has been given by Klemens.[10] Evidently, the thermal resistivity can, in this limit, be represented as a sum of terms arising from defect scattering, Umklapp scattering, and boundary scattering. However, these resistivities are *not* computed in the usual manner as reciprocals of conductivities calculated by averaging the relaxation time for the process concerned over the vibrational spectrum; rather the reciprocal relaxation times themselves are averaged. To evaluate these resistivities, we assume for the relaxation times, as in I (and let $\theta/T \to \infty$):

$$\tau_u^{-1} = B_u T^3 \omega^2; \qquad \tau_B^{-1} = V_s/L. \quad (12)$$

The multiplier B_u in (11) contains the characteristic exponential temperature dependence of Umklapp processes. The quantity L entering into the relaxation time for boundary scattering is some characteristic length of the specimen. In an obvious notation, we may write

$$W = W_Z + W_B + W_u, \quad (13)$$

where W_Z is given by (5) and

$$W_u = \frac{150}{7}\frac{\hbar v_s}{K^2}B_u T^2; \quad W_B = \frac{15 v_s^2}{2\pi^2 KL}\left(\frac{\hbar}{KT}\right)^3. \quad (14)$$

The extension of these results to cases in which the ratios τ_N/τ_u, etc., are not small is tedious but straightforward. It is convenient to introduce the variable t^2

$$t^2 = \frac{\hbar^2}{K^2}\frac{(B_N+B_u)T}{A} = y^2(1+s), \quad (15)$$

where $s = B_u/B_N$. In order to simplify the resulting formulas, we will, in the following, neglect boundary scattering. To facilitate the analysis of the experimental results of Walker and Fairbank,[5] which will be dis-

[10] P. G. Klemens, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 33.

TABLE I. The functions

$$\mathcal{G}_n(y) = \int_0^\infty \frac{x^{2n}}{(x^2+y^2)}\frac{e^x}{(e^x-1)^2}dx$$

are given for $n=1, 2, 3, 4$.

y^2	$\mathcal{G}_1(y)$	$\mathcal{G}_2(y)$	$\mathcal{G}_3(y)$	$\mathcal{G}_4(y)$
0.00	∞	3.2899	25.976	732.48
0.01	15.79	3.1319	25.944	732.23
0.02	10.758	3.0747	25.914	731.97
0.05	6.545	2.9626	25.828	731.19
0.1	4.5096	2.8389	25.692	729.92
0.2	3.0673	2.6764	25.440	727.40
0.5	1.8013	2.3892	24.781	720.09
1.0	1.1766	2.1133	23.862	708.62
2.0	0.74940	1.7911	22.394	687.70
5.0	0.39302	1.3248	19.352	635.73
10.0	0.23128	0.97707	16.205	570.44
20.0	0.13102	0.66942	12.587	480.7
50.0	0.058565	0.36162	7.895	337.8
100.0	0.030802	0.20970	5.006	231.7
200.0	0.015873	0.11519	2.938	144.9
500.0	0.0064811	0.049301	1.325	69.97
1000.0	0.0032646	0.025280	0.6952	37.24
2000.0	0.0016385	0.012811	0.3566	19.39
5000.0	0.0006569	0.005166	0.1449	7.955
10000.0	0.0003287	0.002590	0.07285	4.013

cussed in the next section, it is desirable first to obtain the thermal resistance of pure material containing no defects. This will be called W_u [in the limit of $\tau_u \gg \tau_N$, it is given by (13)] and is computed by setting $\tau_D^{-1} = \tau_B^{-1} = 0$ in Eq. (1).

$$W_u = \frac{150}{7}\frac{\hbar v_s}{K^2}B_u T^2\left(\frac{1+s}{1+25s/7}\right)$$

$$= \frac{6\hbar v_s}{K^2}\frac{(B_u+B_N)T^2}{1+(7/25)B_N/B_u}. \quad (16)$$

If $B_N \ll B_u$, W_u reduces to the quantity referred to as W_p in I. The ratio W/W_u can now be determined:

$$\frac{W}{W_u} = \frac{7\pi^2}{75}\left(1+\frac{25s}{7}\right)$$

$$\times \frac{[\mathcal{G}_3(t)/t^2\mathcal{G}_2^2(t)]+(sy^2)^{-1}[\mathcal{G}_4(t)/t^2\mathcal{G}_2^2(t)]}{1+s\mathcal{G}_3(t)\mathcal{G}_1(t)/\mathcal{G}_2^2(t)+\mathcal{G}_4(t)\mathcal{G}_1(t)/y^2\mathcal{G}_2^2(t)}. \quad (17)$$

This rather formidable formula applies for all values of the strength of the normal processes relative to the defect and Umklapp scatterings. A brief tabulation of the functions $\mathcal{G}_n$ is presented in Table I.

APPLICATION TO SOLID HELIUM

The thermal conductivity of solid helium, containing various proportions of the isotope He^3, has been measured in the range 1.1°K to 2.1°K by Walker and Fairbank.[5] These authors observed that the additional thermal resistivity produced by the isotopic mixture (in comparison with pure He^4) was much too large to be explained by the theory of Klemens, assuming a

random distribution of the isotopes. They attempted to account for their results by supposing that the He³ was arranged on lines in the solid. Subsequently, Sheard and Ziman noted that the thermal resistance due to the isotopes was in order of magnitude agreement with W_Z as given by (5), using Klemens' estimate of A and assuming a random distribution of the isotopes.[6]

In this work, a fit has been made to the data of Walker and Fairbank (Table II of their paper) in the following manner: The thermal resistance of material containing no He³ was attributed to Umklapp processes. It was possible to obtain a good fit to the resistance of the pure material using Eq. (16) with $s = B_u/B_N = 9.12e^{-8.2/T}$. This fit is shown in Fig. 2. It was then possible to choose y^2, utilizing the fact that A must be proportional to $c(1-c)$, where c is the relative concentration of one of the isotopes, so as to obtain a good fit to the ratio W/W_u for the other samples measured. This fit is shown in Fig. 3. It is seen to be possible to account for both the concentration and temperature dependences of the thermal resistivity.

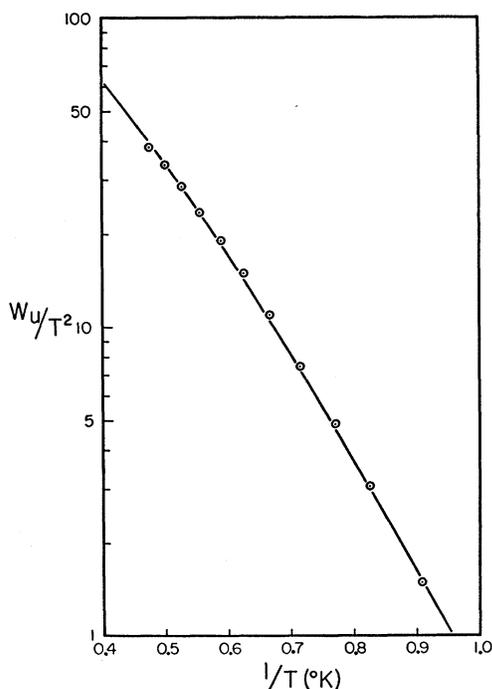The values of the constants appearing in the expressions for the relaxation times used in this fit to the

Fig. 2. The quantity W_u/T^2, where W_u is the thermal resistivity of pure solid He⁴ is given as a function of reciprocal temperature. W_u is measured in units of watt⁻¹ cm °K. The solid curve is obtained from Eq. (16); the circles represent the experimental results of Walker and Fairbank.
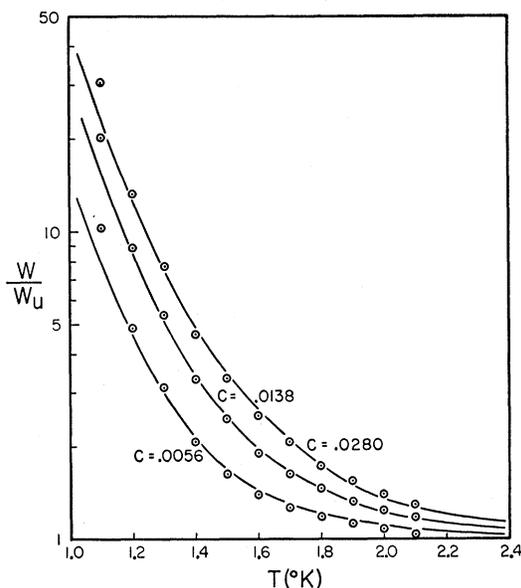

Fig. 3. The ratio of the thermal resistivity, W, of solid helium containing a relative concentration c, of the isotope He³, to the resistivity of pure material, W_u, is shown as a function of temperature. The solid curves represent the predictions of Eq. (17), with values of the constants given in the text. The circles are the experimental results of Walker and Fairbank.

data are

$$A = 7.63c(1-c) \text{ sec}^3,$$

$$B_u = 7.27 \times 10^{-15} e^{-8.2/T} \text{ sec deg}^{-3},$$

$$B_N = 7.97 \times 10^{-16} \text{ sec deg}^{-3}.$$

The value of A used here is approximately three times greater than that obtained from Klemens' formula for mass difference scattering.[9] A more refined calculation of this constant from fundamental considerations would be very desirable if the actual vibrational spectrum of the crystal could be taken into account. However, it seems unlikely that the standard result is in error by this large factor for the long waves which are principally involved. If so, it is possible that the defect scattering includes, in this case, not only simple mass difference scattering but a contribution due to lattice distortion as well. Such distortion would cause additional scattering as discussed in reference 9. Since zero-point motion is important in a crystal with such light atoms, the possibility of existence of lattice distortion around the light isotope should be investigated in detail.