The function is calculated in 10° intervals of β and averaged. K_1 and K_2 are taken from Bozorth[10]; B_1 and B_2, from Kittel.[22] C_{11}, C_{12}, and C_{44} have been measured in this laboratory by Daniels.[23]

An isotropic skin stress of 8×10^9 dynes/cm^2 in iron would yield an average anisotropy of 1.7×10^4 ergs/cm^3 for a fiber axis tilt of 10°. The variation of $f(\perp)-f(\|)$ with β for the condition of isotropic stress is also shown in Fig. 8.

The anisotropy goes roughly as the sine^2 of the angle of tilt. The function $f(\perp)-f(\|)$ averages exactly to zero at a zero angle of tilt; this corresponds to the isotropy produced by normal incidence.

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[23] W. B. Daniels, M.S. thesis, Case Institute of Technology, 1955 (unpublished).

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Model for Lattice Thermal Conductivity at Low Temperatures

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A phenomenological model is developed to facilitate calculation of lattice thermal conductivities at low temperatures. It is assumed that the phonon scattering processes can be represented by frequency-dependent relaxation times. Isotropy and absence of dispersion in the crystal vibration spectrum are assumed. No distinction is made between longitudinal and transverse phonons. The assumed scattering mechanisms are (1) point impurities (isotopes), (2) normal three-phonon processes, (3) umklapp processes, and (4) boundary scattering. A special investigation is made of the role of the normal processes which conserve the total crystal momentum and a formula is derived from the Boltzmann equation which gives their contribution to the conductivity. The relaxation time for the normal three-phonon processes is taken to be that calculated by Herring for longitudinal modes in cubic materials. The model predicts for germanium a thermal conductivity roughly proportional to $T^{-\frac{3}{2}}$ in normal material, but proportional to T^{-2} in single-isotope material in the temperature range 50°–100°K. Magnitudes of the relaxation times are estimated from the experimental data. The thermal conductivity of germanium is calculated by numerical integration for the temperature range 2–100°K. The results are in reasonably good agreement with the experimental results for normal and for single-isotope material.

INTRODUCTION

ALTHOUGH an exact calculation of lattice thermal conductivity is possible in principle, lack of knowledge of crystal vibration spectra and of anharmonic forces in crystals and the difficulty of obtaining exact solutions of the Boltzmann equation are formidable barriers to progress. It is interesting to investigate the consequences of a simple model which is more amenable to calculation. It is assumed in this work that all the phonon scattering processes can be represented by relaxation times which are functions of frequency and temperature. It is further assumed that the material is elastically isotropic and dispersion in the vibrational spectrum is neglected. As a small concession to reality, the relaxation time for normal three phonon processes is taken to be that characteristic of longitudinal modes in a cubic crystal.[1] No distinction is made between longitudinal and transverse phonons.

It is well known that normal processes (scattering processes which conserve the total crystal momentum) cannot by themselves lead to a finite thermal conductivity.[2] Consequently, it cannot be legitimate just to add reciprocal relaxation times for the normal processes (N processes) to those which do not conserve the crystal momentum. Examples of the latter type of process include umklapp processes, impurity scattering, and boundary scattering (we shall designate all such momentum-destroying processes as U processes). U processes tend to return the phonon system to an equilibrium Planck distribution, whereas N processes lead to a displaced planck distribution. An investigation of this point is made in some detail to allow the effect of normal processes to be included more exactly.

Existence of the following scattering processes is assumed: (1) Boundary scattering, described by a constant relaxation time L/c, where c is the velocity of sound and L is some length characteristic of the material. (2) Normal three-phonon processes whose relaxation time is taken to be proportional to $(\omega^2T^3)^{-1}$, where ω is the circular frequency and T is the absolute temperature. For further discussion of this choice, see the Appendix. (3) Impurity scattering, including isotope scattering, whose relaxation time is independent of temperature and proportional to ω^{-4}. (4) Umklapp processes with a relaxation time proportional to $(e^{-\Theta/aT}\omega^2T^3)^{-1}$, where Θ is the Debye temperature and a is a constant characteristic of the vibrational spectrum

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[1] C. Herring, Phys. Rev. **95**, 954 (1954).

[2] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955), Chap. 2.

of the material.[3] For germanium, on account of the extreme dispension in the vibration spectrum,[4] a may be of the order of 8.

Finally, it may be useful to point out that the addition of thermal resistances calculated for separate processes is unjustified at low temperatures because of the strong frequency dependence of the relaxation time. In particular, it is impossible to define a specific thermal resistance due to point defects alone.

NORMAL PROCESSES

The Boltzmann equation in the presence of a temperature gradient is written as

$$\left(\frac{\partial N}{\partial t}\right)_c - \mathbf{c}\cdot\nabla T\frac{dN}{dT}=0, \tag{1}$$

in which N is the distribution function, T the temperature, $\mathbf{c}$ the group velocity, and $(\partial N/\partial t)_c$ the rate of change of N due to collisions. In the second term we may replace N by N_0, the Planck distribution function. The first term is approximated as follows:

$$\left(\frac{\partial N}{\partial t}\right)_c = \frac{N(\boldsymbol{\lambda})-N}{\tau_N}+\frac{N_0-N}{\tau_u}. \tag{2}$$

Here we define τ_N to be the relaxation time for all normal processes and τ_u to be the relaxation time for those processes which do not conserve momentum. τ_u is obtained by adding reciprocal relaxation times for the appropriate processes. N_0 is the Planck distribution and $N(\boldsymbol{\lambda})$ is the displaced Planck distribution to which the normal processes tend.[3]

$$N(\boldsymbol{\lambda})=\left[\exp\left(\frac{\hbar\omega-\boldsymbol{\lambda}\cdot\mathbf{k}}{KT}\right)\right]^{-1}=N_0+\frac{\boldsymbol{\lambda}\cdot\mathbf{k}}{KT}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}. \tag{3}$$

If we define $n_1=N-N_0$, the Boltzmann equation (1) can be written as

$$-\frac{\hbar\omega}{KT^2}\mathbf{c}\cdot\nabla T\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}+\frac{\boldsymbol{\lambda}\cdot\mathbf{k}}{\tau_N KT}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2} -\left(\frac{1}{\tau_N}+\frac{1}{\tau_u}\right)n_1=0. \tag{4}$$

We define a combined relaxation time τ_c by

$$\tau_c^{-1}=\tau_N^{-1}+\tau_u^{-1}. \tag{5}$$

We express n_1 as follows:

$$n_1=-\alpha\mathbf{c}\cdot\nabla T\frac{\hbar\omega}{KT^2}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}, \tag{6}$$

where $\alpha(k)$ is a total relaxation time. It is desired to determine α in terms of τ_c and τ_N. Upon using (6), the thermal conductivity κ is easily found to be

$$\kappa=\frac{3}{(2\pi)^3}\int c^2\cos^2\theta\,\alpha(k)C_{\text{ph}}(k)d^3k. \tag{7}$$

The factor 3 comes from the three contributing branches of the vibrational spectrum. (At the low temperatures we are interested in, the optical modes will not be excited. In any case their contribution to the thermal conductivity is limited by their low group velocity.) In (7), C_{ph} is the phonon specific heat:

$$C_{\text{ph}}=\frac{\hbar^2\omega^2}{KT^2}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}. \tag{8}$$

Substitution of (5) and (6) into (4) yields

$$\frac{\hbar\omega\alpha}{\tau_c T}\mathbf{c}\cdot\nabla T+\frac{\boldsymbol{\lambda}\cdot\mathbf{k}}{\tau_N}=\frac{\hbar\omega}{T}\mathbf{c}\cdot\nabla T. \tag{9}$$

Since $\boldsymbol{\lambda}$ must be a constant vector in the direction of the temperature gradient, it is convenient to define a parameter β with the dimensions of a relaxation time by

$$\boldsymbol{\lambda}=-(\hbar/T)\beta c^2\nabla T. \tag{10}$$

Since $\mathbf{k}=\mathbf{c}\omega/c^2$, we have

$$\boldsymbol{\lambda}\cdot\mathbf{k}=-(\hbar\omega/T)\beta\mathbf{c}\cdot\nabla T, \tag{10a}$$

so that (9) simplifies to

$$\frac{\alpha}{\tau_c}-\frac{\beta}{\tau_N}=1,\quad\text{or}\quad \alpha=\tau_c(1+\beta/\tau_N). \tag{11}$$

If we make use of the assumed isotropy, the thermal conductivity is found to be

$$\kappa=\frac{c^2}{2\pi^2}\int\tau_c\left(1+\frac{\beta}{\tau_N}\right)C_{\text{ph}}k^2dk. \tag{12}$$

The combined relaxation time appears in (12) multiplied by the factor $(1+\beta/\tau_n)$ which expresses the correction due to the nature of the distribution $N(\boldsymbol{\lambda})$. It is now necessary to determine β. To do this, we utilize the fact that the normal processes conserve momentum. The rate of change of the total phonon momentum due to N processes is set equal to zero. We express this as

$$\int\left(\frac{\partial N}{\partial t}\right)_N\mathbf{k}d^3k=\int\frac{N(\boldsymbol{\lambda})-N}{\tau_N}\mathbf{k}d^3k=0. \tag{13}$$

Substitution of (3) and (6) into (13) leads to

$$\int\frac{e^{\hbar\omega/KT}}{[e^{\hbar\omega/KT}-1]^2}\left[\frac{\hbar\omega}{KT^2}\alpha\mathbf{c}\cdot\nabla T+\frac{\boldsymbol{\lambda}\cdot\mathbf{k}}{KT}\right]\frac{\mathbf{k}}{\tau_N}d^3k=0. \tag{14}$$

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[3] P. G. Klemens, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 198.

[4] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **108**, 894 (1957).

When the expression (10a) for $\boldsymbol{\lambda}\cdot\mathbf{k}$ is substituted into (14), the equation becomes

$$\int \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}\frac{\hbar\omega}{KT^2}(\mathbf{c}\cdot\nabla T)(\alpha-\beta)\frac{\mathbf{c}\omega}{\tau_N c^2}d^3k.$$

If we introduce the variable $x=\hbar\omega/KT=\hbar ck/KT$, we find that

$$\int_0^{\Theta/T}\frac{e^x}{(e^x-1)^2}(\alpha-\beta)\frac{x^4}{\tau_N}dx=0, \tag{15}$$

since α is a function of the magnitude of $\mathbf{k}$ only. Θ is the Debye temperature. We can insert α from (11) and solve for β which is independent of x:

$$\beta=\int_0^{\Theta/T}\frac{\tau_c}{\tau_N}\frac{e^x}{(e^x-1)^2}x^4dx \Bigg/ \int_0^{\Theta/T}\frac{1}{\tau_N}\left(1-\frac{\tau_c}{\tau_N}\right)\frac{e^x}{(e^x-1)^2}x^4dx. \tag{16}$$

When β is computed in this way and is substituted into (12), the thermal conductivity is determined. We observe that in the limit $\tau_u\rightarrow\infty$ (no U processes), τ_c approaches τ_N and β becomes infinite. Consequently κ becomes infinite as required. When τ_N becomes large, we see from (12) and (16) that the thermal conductivity is determined principally by τ_u and that addition of reciprocal relaxation times is justified in this limit.

CALCULATION OF THE THERMAL CONDUCTIVITY

Even with the extreme simplifications made in this model, it does not appear possible to evaluate the basic integrals analytically. Approximate evaluations can be made which retain the essential features of the theory, in particular the temperature dependence. Results based on numerical integration are presented in the next section.

The thermal conductivity is obtained from Eqs. (12) and (16) employing the relaxation times discussed in the introduction. We can write,

$$\tau_u^{-1}=A\omega^4+B_1T^3\omega^2+c/L, \tag{17}$$

where the term $A\omega^4$ represents the scattering by point impurities or isotopes; the term $B_1T^3\omega^2$ includes the umklapp processes (B_1 contains the exponential temperature factor $e^{-\Theta/aT}$); and c/L represents the boundary scattering. Since measurements of the thermal conductivity of germanium have been made on a sample almost isotopically pure,[5] special attention will be given to the case $A=0$. Similarly

$$\tau_N^{-1}=B_2T^3\omega^2, \tag{17a}$$

where B_2 is independent of temperature. The combined relaxation time is

$$\tau_c^{-1}=A\omega^4+(B_1+B_2)T^3\omega^2+c/L. \tag{18}$$

We then write

$$\kappa=\frac{K}{2\pi^2c}(I_1+\beta I_2), \tag{19}$$

where

$$I_1=\int_0^{K\Theta/\hbar}\tau_c\frac{\hbar^2\omega^2}{K^2T^2}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}\omega^2d\omega, \tag{20}$$

and

$$I_2=\int_0^{K\Theta/\hbar}\frac{\tau_c}{\tau_N}\frac{\hbar^2\omega^2}{K^2T^2}\frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT}-1)^2}\omega^2d\omega. \tag{21}$$

Consider I_1. Introduce the dimensionless variable x as in (15). Equation (20) becomes, on substitution of (18),

$$I_1=\left(\frac{KT}{\hbar}\right)^3\int_0^{\Theta/T}\frac{x^4}{(Dx^4+Ex^2+c/L)}\frac{e^x}{(e^x-1)^2}dx, \tag{22}$$

in which $D=A(KT/\hbar)^4$; $E=(B_1+B_2)T^3(KT/\hbar)^2$. At very low temperatures, D and E are much smaller than c/L, so that the denominator may be expanded. The upper limit may be set equal to infinity. To first order in D and E, we obtain

$$I_1=\frac{4\pi^4}{15}\frac{L}{c}\left(\frac{KT}{\hbar}\right)^3\left[1-\frac{20\pi^2}{7}\frac{EL}{c}-16\pi^4\frac{DL}{c}\right],$$

which gives rise to a thermal conductivity (neglecting the βT_2 term).

$$\kappa=\frac{2K\pi^2L}{15c^2}\left(\frac{KT}{\hbar}\right)^3\left[1-16A\left(\frac{\pi KT}{\hbar}\right)^4\frac{L}{c}-\frac{20}{7}(B_1+B_2)T^3\left(\frac{\pi KT}{\hbar}\right)^2\frac{L}{c}\right]. \tag{23}$$

Because of the strong dependence of D and E on the temperature, at higher temperatures the situation is reversed, and c/L is effectively small. If D is large, the isotope scattering is very effective for short waves and we may evaluate (22) approximately by replacing $x^2e^x/(e^x-1)^2$ by unity. Thus

$$I_1=\frac{\pi}{2(ED)^{\frac{1}{2}}}\left(\frac{KT}{\hbar}\right)^3\left[1+\frac{2}{E}\left(\frac{cD}{L}\right)^{\frac{1}{2}}\right]^{-\frac{1}{2}}$$
$$=\frac{\pi}{2[A(B_1+B_2)]^{\frac{1}{2}}T^{\frac{3}{2}}}\left[1+\frac{2(cA/L)^{\frac{1}{2}}}{(B_1+B_2)T^3}\right]^{-\frac{1}{2}}. \tag{24}$$

At temperatures above perhaps 30°K the size dependence may be regarded as a correction, so that we can expand the bracket in (24), retaining only the first term:

$$I_1=\frac{\pi}{2}\frac{1}{[A(B_1+B_2)]^{\frac{1}{2}}T^{\frac{3}{2}}}\left[1-\frac{(cA/L)^{\frac{1}{2}}}{(B_1+B_2)T^3}\right]. \tag{25}$$

If we anticipate that the term βI_2 in (19) will prove to be only a reasonably small correction, we observe from

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[5] T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

(25) that the thermal conductivity in the region just beyond the low-temperature maximum will be proportional to $T^{-\frac{3}{2}}$, unless B_2 is so much smaller than B_1 that an exponential temperature dependence $e^{\Theta/2aT}$ will be observed.

If A is very small, as will be the case for a chemically pure single crystal containing only one isotope, this result must be modified. We cannot use the isotope contribution to render the integral (22) convergent. If we set $D=0$ in (22), we then have

$$I_1=\left(\frac{KT}{\hbar}\right)^3\frac{1}{E}\int_0^{\Theta/T}\frac{x^4}{x^2+c/LE}\frac{e^x}{(e^x-1)^2}dx. \tag{26}$$

This integral is somewhat simpler than before, and we shall retain the finite Θ/T. Even at temperatures for which the boundary scattering may still be regarded as small, the integral (26) does not possess an expansion in integral powers of c/LE. Instead it can be shown that, to a reasonable approximation,

$$\begin{aligned}I_1&=\left(\frac{KT}{\hbar}\right)^3\frac{1}{E}\left[\tfrac{1}{3}\pi^2-e^{-\Theta/T}\left(\frac{\Theta^2}{T^2}+\frac{2\Theta}{T}+2\right)-\frac{\pi}{2}\left(\frac{c}{LE}\right)^{\frac{1}{2}}\right]\\&=\frac{K\pi^2}{3\hbar(B_1+B_2)T^2}\left\{1-\frac{3e^{-\Theta/T}}{\pi^2}\left(\frac{\Theta^2}{T^2}+\frac{2\Theta}{T}+2\right)\right.\\&\qquad\left.-\frac{3\hbar}{2\pi KT^{\frac{5}{2}}}\left[\frac{c}{L(B_1+B_2)}\right]^{\frac{1}{2}}\right\}.\end{aligned} \tag{27}$$

It is seen from (27) that the thermal conductivity in isotopically pure materials should depend on temperature as T^{-2} beyond the low-temperature maximum. This means it should exhibit a sharper falloff in temperature. The size-dependent part of the conductivity is actually the same in (25) and (27) and has the temperature dependence $T^{-9/2}$ predicted by Herring.[1] However, the size dependence is relatively less important in the isotopically pure material because the over-all conductivity is higher.

We must now calculate I_2 and β. Anticipating the relatively small effect of these terms, we neglect their size dependence. This will not be valid at very low temperatures. We have, for normal material,

$$\tau_c/\tau_N=B_2T^3\omega^2/[A\omega^4+(B_1+B_2)T^3\omega^2+c/L],$$

$$I_2=B_2T\left(\frac{KT}{\hbar}\right)^3\int\frac{x^4}{[(K^2Ax^2/\hbar^2)+(B_1+B_2)T]}\times\frac{e^x}{(e^x-1)^2}dx. \tag{28}$$

This integral can be evaluated in the same fashion as (26).

$$I_2=\frac{\pi^2B_2T^3}{3A}\left(\frac{KT}{\hbar}\right)\left[1-\frac{3}{2\pi}\frac{\hbar}{K}\left(\frac{(B_1+B_2)T}{A}\right)^{\frac{1}{2}}\right]. \tag{29}$$

According to Eq. (16), $\beta=(\hbar/KT)^3I_2/I_3$, where

$$I_3=B_2T^3\left(\frac{KT}{\hbar}\right)^2\int_0^{\Theta/T}\frac{A\omega^4+B_1T^3\omega^2+c/L}{[A\omega^4+(B_1+B_2)T^3\omega^2+c/L]}\times\frac{x^6e^x}{(e^x-1)^2}dx. \tag{30}$$

We approximate this integral as follows:

$$I_3=B_2T^3\left(\frac{KT}{\hbar}\right)^2\int_0^{\infty}\frac{x^6e^x}{(e^x-1)^2}dx=\frac{16\pi^6}{21}B_2T^3(KT/\hbar)^2. \tag{31}$$

These are important corrections which have to be made to I_2 and I_3 to allow for a finite value of Θ/T. These are easily obtained and will not be presented here. Thus we find

$$\beta=\frac{7}{16A}\left(\frac{\hbar}{\pi KT}\right)^4\left\{1-\frac{3}{2\pi}\frac{\hbar}{K}\left[\frac{(B_1+B_2)T}{A}\right]^{\frac{1}{2}}\right\}. \tag{32}$$

Then

$$\beta I_2=\frac{7B_2\hbar^3}{48\pi^2A^2K^3}\left\{1-\frac{3}{\pi}\frac{\hbar}{K}\left[\frac{(B_1+B_2)T}{A}\right]^{\frac{1}{2}}\right\}.$$

This result can now be combined with (25) and (19) to obtain the total thermal conductivity.

$$\kappa=\frac{K}{4\pi cT^{\frac{3}{2}}}\frac{1}{[A(B_1+B_2)]^{\frac{1}{2}}}\left[1-\frac{(cA/L)^{\frac{1}{2}}}{(B_1+B_2)T^3}\right]+\frac{7B_2\hbar^3}{96\pi^4K^2cA^2}\left\{1-\frac{3}{\pi}\frac{\hbar}{K}\left[\frac{(B_1+B_2)T}{A}\right]^{\frac{1}{2}}\right\}. \tag{33}$$

Thus, the thermal conductivity of a large sample of material in the temperature region considered deviates from $T^{-\frac{3}{2}}$ by a correction roughly independent of temperature.

For a chemically and isotopically pure material, we have

$$I_2=\frac{B_2}{B_1+B_2}\left(\frac{KT}{\hbar}\right)^3\int_0^{\infty}\frac{x^4e^x}{(e^x-1)^2}dx=\frac{4\pi^4}{15}\frac{B_2}{(B_1+B_2)}\left(\frac{KT}{\hbar}\right)^3, \tag{34}$$

$$I_3=\frac{B_1B_2T^3}{B_1+B_2}\left(\frac{KT}{\hbar}\right)^2\int\frac{x^6e^x}{(e^x-1)^2}dx=\frac{16\pi^6}{21}\frac{B_1B_2T^3}{(B_1+B_2)}\left(\frac{KT}{\hbar}\right)^2. \tag{35}$$

Consequently,

$$\beta = 7\hbar^2/(20\pi^2 K^2 B_1 T^5).$$

The thermal conductivity of the pure material is then

$$\kappa = \frac{K^2}{6\hbar(B_1+B_2)cT^2}\left[1-\frac{3}{\pi^2}e^{-\Theta/T}\left(\frac{\Theta^2}{T^2}+\frac{2\Theta}{T}+2\right)\right.$$
$$\left.-\frac{3\hbar}{2\pi K T^{\frac{5}{2}}}\left[\frac{c}{L(B_1+B_2)}\right]^{\frac{1}{2}}+\frac{7}{25}\frac{B_2}{B_1}\right]. \qquad (36)$$

At very low temperatures, we retain the size dependence, treat the normal processes as small, and obtain

$$\beta = L/c; \quad \beta I_2 = (16\pi^6/21)B_2 T^3 (KT/\hbar)^5 (L/c)^2. \qquad (37)$$

We find by combining (37) with (23) in (19), that

$$\kappa = \frac{2K\pi^2}{15}\frac{L}{c^2}\left(\frac{KT}{\hbar}\right)^3\left[1-16A\left(\frac{\pi KT}{\hbar}\right)^4\frac{L}{c}\right.$$
$$\left.-\frac{20}{7}B_1 T^3\left(\frac{\pi KT}{\hbar}\right)^2\frac{L}{c}\right], \qquad (38)$$

so that the normal processes do not contribute at the lowest temperature.

COMPARISON WITH EXPERIMENT FOR GERMANIUM

There have been several measurements of the thermal conductivity of germanium. Some of these works are listed below.[5–8] Slack[9] has emphasized the importance of isotope scattering.

Qualitatively, we can explain the shape of the observed thermal conductivity curve at low temperatures as follows: At the very lowest temperatures, boundary scattering predominates, and the thermal conductivity goes as T^3. Even at 2°K the T^7 deviations from boundary scattering in normal material are appreciable, so that pure T^3 behavior is not observed. The isotope scattering rapidly becomes important as it becomes easier to create higher frequency phonons which are scattered efficiently by point impurities. Consequently, the thermal conductivity reaches a maximum and then declines. As the temperature increases further, normal three-phonon scattering and umklapp scattering become important, and come to dominate the isotope scattering. In the region from 40 to 100°K the conductivity of a large sample should be proportional to $T^{-\frac{3}{2}}$. It is likely that observed deviations from this law ($T^{-1.3}$ is reported by White and Woods) are caused by the dying out of boundary scattering. At higher temperatures, the simple model of this work ceases to apply as Θ/T decreases and the relaxation times for all phonon-phonon scattering processes become proportional to T^{-1}.

In isotopically pure material the T^3 behavior characteristic of predominant boundary scattering persists to 5 or 6°K. Three-phonon scattering and umklapp processes gradually set in, but the conductivity reaches a considerably higher maximum than normal material. The falloff from the maximum is steeper, and T^{-2} behavior is observed from 40 to 100°K.[5]

In order to make a more detailed comparison of theory and experiment, we have evaluated the basic parameters of the theory from the experimental data of Geballe and Hull.[5] This was done as follows: From the coefficient of the T^3 term in the thermal conductivity of their enriched Ge^{74} sample, the quantity c/L can be determined. They report (using $c = 3.50\times10^5$ cm sec^{-1}) that $L = 0.180$ cm. We assume that the residual isotope scattering in their enriched material can be neglected at 75°K, and from (36) (neglecting the term proportional to B_2/B_1) we determine a value for (B_1+B_2). In doing this, we assume $\Theta = 375$°K, a value close to that obtained by Marcus and Kennedy.[10] We obtain in this way $(B_1+B_2) = 2.77\times10^{-23}$ sec deg^{-3}. The value of A was determined by numerically integrating (22) for $T = 75$°K, using the previously determined (B_1+B_2) with different choices of A until agreement with the result of Geballe and Hull for normal Ge was obtained. The correction $K\beta I_2/2\pi^2 c$ was again neglected. A was found to be 2.57×10^{-44} sec^3.

Klemens has calculated the relaxation time due to isotope scattering.[11] He obtained

$$\tau^{-1} = \frac{V_0}{4\pi c^3}\sum_i f_i[1-(M_i/M)]^2\omega^4 = A\omega^4, \qquad (39)$$

where V_0 is the volume per atom, M_i is the mass of an atom, f_i is the fraction of atoms with mass M_i, and M is the average mass of all atoms. The quantity A was computed from (39) using a value for the sum given by Slack.[9] The result is $A = 2.40\times10^{-44}$ sec^3. The agreement with the result deduced from the experimental data is very striking.

The values of the constants A, (B_1+B_2), and c/L determined above were used to calculate the thermal conductivities of normal Ge and single-isotope Ge in the range 2°–100°K by numerical integration according to Eqs. (19) and (22). The correction $K\beta I_2/2\pi^2 c$ was neglected throughout, and (B_1+B_2) was taken to be independent of temperature, although neither assumption is really valid. The results are shown in Fig. 1, where they are compared with some points read from the graph of Geballe and Hull.[5] It is seen the agreement is quite good except in the vicinity of the maximum. In the case of the single-isotope curve, a small amount of residual isotope scattering in the enriched sample

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[6] Carruthers, Geballe, Rosenberg, and Ziman, Proc. Roy. Soc. (London) **A238**, 502 (1957).

[7] G. K. White and S. B. Woods, Phys. Rev. **103**, 569 (1956).

[8] H. M. Rosenberg, Proc. Phys. Soc. (London) **A67**, 837 (1954).

[9] G. A. Slack, Phys. Rev. **105**, 829 (1957).

[10] P. M. Marcus and A. J. Kennedy (to be published).

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

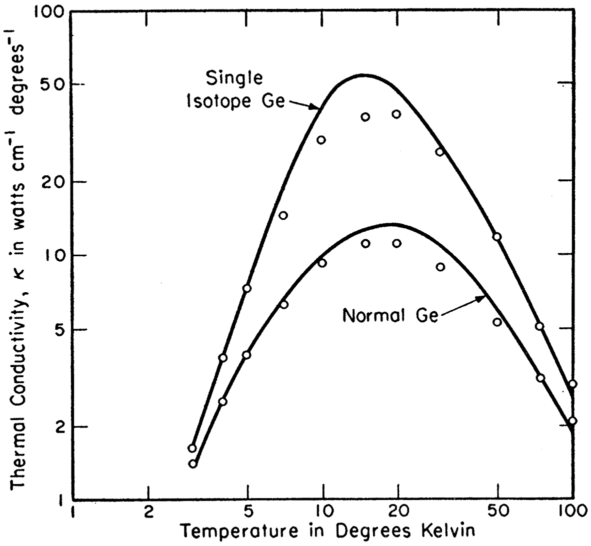

FIG. 1. Thermal conductivity of germanium. The solid lines are the theoretical curves whose computation is described in the text. The open circles represent experimental points read from the graph of Geballe and Hull.

could easily account for much of the discrepancy near the maximum. The effect of the other approximations mentioned above, which have their most serious effect in this region, is to give an underestimate of the thermal conductivity. It is significant that the theory gives correctly the very-low-temperature deviations of the conductivity of the normal material from the T^3 law, which are important even at the lowest temperature shown. These deviations are due to isotope scattering, and the fit indicates that the isotope contribution is given correctly by this simple theory at low temperatures.

The correction $\Delta\kappa = K\beta I_2/2\pi^2 c$ has been estimated by numerical integration for $T=75$°K for the normal material. An overestimate is made if we set $B_2=B_1+B_2$ in (28). It is found on this basis that $\Delta\kappa = 0.3$ watt cm^{-1} deg^{-1}, about 10% of the observed value of κ. The correction to the conductivity of the single-isotope material might be more serious, but cannot be reliably estimated since it depends essentially on the unknown ratio B_2/B_1.

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APPENDIX. CHOICE OF PHONON-PHONON RELAXATION TIMES

Herring[1] has established that the relaxation time of a single low-energy mode of wave vector **k** via three-phonon scattering processes depends on wave number and temperature as

$$\tau^{-1}(k) = k^s T^{5-s}, \tag{A1}$$

where s is an exponent determined by crystal symmetry. For reasons of mathematical simplicity, we have chosen $s=2$ which is characteristic of longitudinal acoustic modes in a cubic crystal. A short calculation leads to the result that for $s<3$, the thermal conductivity of single-isotope material will be proportional to T^{-2}, independently of s, beyond the low-temperature maximum. The restriction $s<3$ is necessary so that the integral (20) will converge if these scattering processes alone are considered. However, if isotope scattering is included, the exponent of the temperature dependence will depend on s. We have already seen in Eq. (24) that if $s=2$, the thermal conductivity in the presence of strong isotope scattering goes as $T^{-\frac{3}{2}}$ .If we choose instead $s=1$, a similar calculation shows that the temperature dependence is $T^{-\frac{4}{3}}$. Of course, in a detailed comparison of theory and experiment, boundary scattering cannot be neglected.

It should be pointed out that the relation (A1) is expected to hold only for phonons whose energies are small compared to KT. The extent of the agreement between theory and experiment suggests that at least in some average sense, (A1) is valid for the bulk of the phonons participating in thermal conduction in the range 40–100°K.