

Analysis of Lattice Thermal Conductivity*

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An analysis of thermal conductivity is presented which differs from that of Klemens and of Callaway in that it considers explicitly the conduction by both transverse and longitudinal phonons. This approach is then used to provide a very good fit to the data on silicon from 1.7 to 1300°K and on germanium from 1.7 to 1000°K, and is also used to fit the data on isotropically pure germanium. A comparison of the analysis with that due to Callaway shows that the same results are obtained in the impurity scattering and boundary scattering regions. A discussion of the approximations used in the various analyses is included. A more complete expression for the umklapp scattering relaxation time, valid for materials with a very disperse transverse acoustic phonon spectrum, is derived in an appendix. The question of the validity of the addition of inverse relaxation times and the coupling due to normal three-phonon processes is considered in another appendix.

I. INTRODUCTION

THE thermal conductivity of materials in which the heat is carried by phonons, has been qualitatively understood for many years. According to the early work of Debye and Peierls, the following behavior, which is in good agreement with experiment, is to be expected: At the lowest temperatures the thermal conductivity κ depends on the size and shape of the crystal (or crystallites) and increases with temperature about as the specific heat. The thermal conductivity reaches a maximum and at temperatures above this maximum κ is limited by the scattering of phonons by phonons and is characteristic of the material. Near the maximum, κ is sensitive to the imperfections and impurities in the material.

In the past few years attempts have been made to refine and expand the theory. In order to make qualitative calculations, a number of assumptions must be introduced into the general theory. The usual approach^{1,2} is to use a relaxation time approximation in the Boltzmann equation and then calculate the scattering cross section by perturbation techniques. Further, it is often necessary to assume an isotropic, Debye-like phonon spectrum consisting of one (average) acoustic branch. Under these conditions it is often possible to find reasonably good agreement between theory and experiment in certain temperature ranges.

One of the difficult problems in this approach is that of developing expressions for the relaxation times, especially those due to three-phonon interactions.^{1,3,4} The frequency and temperature dependence of the three-phonon relaxation times is strongly dependent on the actual phonon branch and of the dispersion in the phonon spectrum so that approximated expressions may only have validity for certain limited phonons or

for a limited temperature range.⁴ Furthermore, these scattering processes are not necessarily independent and the simple addition of scattering probabilities may not be justifiable.³

Recently, Callaway⁵ presented a formulation of the problem. By assuming a Debye phonon spectrum and making several assumptions as to the form of the three-phonon scattering times, he derived an expression for the low-temperature thermal conductivity in terms of several constants which represent the strength of the three-phonon scattering. These constants are contained in rather formidable integrals so that extensive numerical integration programs are needed. This formulation has been successful in fitting the data on a number of materials at low temperatures.⁵⁻¹⁵

For several materials such as silicon and germanium in which the thermal conductivity has been extensively studied, detailed information about the phonon spectrum¹⁶⁻¹⁸ and phonon density-of-states distribution¹⁹ is now available. Using these data, it is conceivable that some of the restricting assumptions might be eliminated. This is what has been attempted in this work.

The approach used here is to divide the heat flow into that carried by transverse phonons and longitudinal phonons. While it is straightforward to obtain the

⁵ J. Callaway, Phys. Rev. **113**, 1046 (1959).

⁶ R. O. Pohl, Phys. Rev. **118**, 1499 (1960).

⁷ J. Callaway and H. C. von Baeyer, Phys. Rev. **100**, 1149 (1960).

⁸ A. M. Toxen, Phys. Rev. **122**, 450 (1961).

⁹ J. Callaway, Phys. Rev. **122**, 787 (1961).

¹⁰ J. C. Thompson and B. A. Younglove, J. Phys. Chem. Solids **20**, 146 (1961).

¹¹ M. V. Klein, Phys. Rev. **123**, 1977 (1961).

¹² M. G. Holland and L. J. Neuringer, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 475.

¹³ B. K. Agrawal and G. S. Verma, Phys. Rev. **126**, 24 (1962).

¹⁴ B. K. Agrawal and G. S. Verma, Physica **28**, 599 (1962).

¹⁵ C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

¹⁶ B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

¹⁷ B. N. Brockhouse, Phys. Rev. Letters **2**, 256 (1959).

¹⁸ H. Palevsky, D. J. Hughes, W. Kley, and E. Tunkels, Phys. Rev. Letters **2**, 258 (1959).

¹⁹ J. C. Phillips, Phys. Rev. **113**, 147 (1959).

* A preliminary account of this work has been given in Bull. Am. Phys. Soc. **8**, 207 (1963).

¹ For a general review of the subject, see P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

² P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

³ P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

⁴ C. Herring, Phys. Rev. **95**, 954 (1954).

TABLE I. Relaxation times. In these expressions the B 's are constants, L = the equivalent sample size where $l_1 l_2$ is the sample cross section; F is a geometric factor, V is the atomic volume, f_i is the atomic fraction of the i th impurity whose mass is M_i , M is the mass of an atom of the host lattice, $\Delta M = M - M_i$, v_s is an average phonon velocity, ω_2 is the zone boundary value of the transverse acoustical mode.

Scattering process	Inverse relaxation time
Crystalline boundaries ^a	$\tau_b^{-1} = v_s/LF, L = \frac{2}{\pi^2}(l_1 l_2)^{1/2}$
Impurities (mass difference) ^b	$\tau_I^{-1} = A\omega^4, A = (V\Gamma)/4\pi v_s^3$ $\Gamma = \sum_i f_i \left(\frac{\Delta M}{M}\right)^2$
Three phonon	
N process ^c	
Longitudinal	$\tau_{LN}^{-1} = B_L \omega^2 T^3$
Transverse	$\tau_{TN}^{-1} = B_T \omega T^4$
Longitudinal	$\tau_{LN}^{-1} = B'_L \omega^2 T$
Transverse	$\tau_{TN}^{-1} = B'_T \omega T$
U processes	
Klemens ^d	$\tau_U^{-1} = B_U \omega^2 T^3 \exp(-\theta/\alpha T)$
Klemens ^e	$\tau_U^{-1} = B_U \omega T^3 \exp(-\theta/\alpha T)$
Dispersive Transverse	$\tau_{TU}^{-1} = B_{TU} \omega^2 / \sinh x, \omega_1 \leq \omega \leq \omega_2,$ $x = \hbar\omega/kT$
	$= 0, \omega < \omega_1$
Callaway ^f	$\tau_U^{-1} = B_U \omega^2 T^3$
Klemens ^g	$\tau_U^{-1} = B' \omega^2 T$ — high temperature

^a H. B. G. Casimir, *Physica* 5, 595 (1938) and Refs. 24 and 25.

^b P. G. Klemens, *Proc. Phys. Soc. (London)* 68, 1113 (1955).

^c Ref. 4.

^d Ref. 3.

^e Ref. 1.

^f Ref. 5.

^g Ref. 1.

propagation velocity of the two modes from elastic constant measurements,²⁰ this would not be sufficient reason to attempt this type of separation. Greater knowledge of the phonon spectrum is needed.

The materials studied, germanium and silicon, have very disperse transverse acoustic modes,¹⁶⁻¹⁸ and this fact allows the development of an expression for certain three-phonon scattering processes, valid over a large range of temperature and phonon frequency. However, the results indicate that the separation into transverse and longitudinal modes is the more important aspect of this work and this approach can give insight into insufficiencies in the existing thermal conductivity formulations even when details of the phonon spectrum and phonon scattering processes are lacking.

II. THEORY

To develop an expression for the lattice thermal conductivity of a material one begins with a Boltzmann equation.^{1,2,3,21,22} The solution of this integral equation is then approximated either by the use of a variational

²⁰ See, for example, J. deLaunay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

²¹ J. M. Ziman, *Electrons and Phonons* (The Clarendon Press, Oxford, 1960), Chap. VI.

²² R. Peierls, *Quantum Theory of Solids* (The Clarendon Press, Oxford, 1955).

principle and trial functions, or by the use of the relaxation time concept. There are problems in both approaches and these have been discussed in detail elsewhere.^{1,2,21} We use the relaxation time approximation²³ in which the phonon scattering is expressed in terms of the relaxation time $\tau(\mathbf{q},\lambda)$ for the phonon (\mathbf{q},λ) with \mathbf{q} the wave vector and λ the polarization.

If \hat{z} is a unit vector along a principal crystal axis and the temperature gradient ΔT is along \hat{z}

$$\kappa_i = \frac{1}{(2\pi)^3} \sum_{\lambda} \int (\mathbf{v}_{q,\lambda} \cdot \hat{z})^2 \tau(\mathbf{q},\lambda) C_{ph}(\mathbf{q},\lambda) d\mathbf{q}. \quad (1)$$

Here $\mathbf{v}_{q,\lambda}$ is the phonon velocity and C_{ph} is the specific heat per normal mode for frequency ω ,

$$C_{ph}(x) = kx^2 e^x \{e^x - 1\}^{-2}. \quad (2)$$

Here $x = \hbar\omega/kT$ and the phonon spectrum relates ω to q .

For the case of an isotropic \mathbf{v}_q ,

$$\kappa = \frac{4\pi}{3} \frac{1}{(2\pi)^3} \sum_{\lambda} \int_q v_{q,\lambda}^2 \tau(q,\lambda) C_{ph}(q,\lambda) f(q,\lambda) dq, \quad (3)$$

where $f(q,\lambda)$ is a phonon distribution function which is independent of direction.

In the Debye limit, $\omega = vq$, $f(q,\lambda) dq = q^2 dq = (\omega^2/v^3) d\omega$, and we obtain

$$\kappa = \frac{1}{3} \left(\frac{1}{2\pi^2} \right) \sum_{\lambda} \int_0^{\omega_{0,\lambda}} \frac{\tau(\omega,\lambda)}{v_{\omega,\lambda}} C_{ph}(\omega,\lambda) \omega^2 d\omega, \quad (4)$$

where $\omega_{0,\lambda}$ is the maximum frequency for the phonon branch λ .

When the scattering processes are independent, the scattering probabilities are additive so that

$$\tau^{-1} = \sum_j \tau_j^{-1}, \quad (5)$$

where each τ_j is the relaxation time for a single scattering process. The τ_j 's are normally obtained by perturbation techniques. The important scattering times are listed in Table I.

Several points should be made concerning these relaxation times. For the boundary scattering term, the factor F represents a correction due to both the smoothness of the surface and the finite length to thickness ratio of the sample.^{24,25} In general, all the approaches lead to the same expression for thermal conductivity at the lowest temperatures. The form of τ_b usually gives agreement between theory and experiment of better than 50%, and in many analyses, the value of F is adjusted to give an exact fit at low temperatures.

²³ The question of the validity of the relaxation time for a single mode will not be discussed here.

²⁴ R. Berman, F. E. Simon, and J. M. Ziman, *Proc. Roy. Soc. (London)* A220, 171 (1953).

²⁵ R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc. (London)* A231, 130 (1955).

For τ_I the scattering parameter Γ is for mass-difference scattering alone. For other types of impurity scattering, such as that due to strain fields or changes in the elastic constants of the interatomic linkages due to the point imperfection, the form of Γ is changed, and in some cases the frequency dependence is altered as well.^{2,26} In this study the impurity scattering is due solely to the various isotopes present in the materials, and the mass-difference term will be the only one considered.

Since three-phonon processes arise due to the anharmonic nature of the lattice energy and the discrete nature of the lattice structure, details of the dispersion of the phonon spectrum must be known in order to derive the relaxation times. Herring,⁴ in obtaining the expressions for N processes, has considered the crystal class explicitly so that the τ_N given in the Table are correct for the materials studied here but are not generally valid. A smooth transition from the low-temperature to the high-temperature form of τ_N is also expected.

Phonon dispersion is equally important for the U -process relaxation times but the forms of τ_U normally are derived without this consideration.^{1,3} The form τ_{TU} shown in Table I is derived in Appendix A and holds for materials such as germanium and silicon in which the frequency of the transverse acoustic branch becomes independent of wave vectors at a point about halfway towards the crystal zone. The limit on the frequency represents the fact that the low-frequency phonons ($\omega < \omega_1$) seldom take place in processes in which the sum of the wave vectors is larger than a vector of the reciprocal lattice, a condition necessary for U processes.¹

For completeness, several other possible mechanisms should be mentioned. In semiconductors at low temperatures there are several possibilities for scattering due to the electronic nature of the impurity centers. These mechanisms have been examined by several workers,²⁷⁻³⁰ but in pure samples they are not expected to be important.

At high temperatures there is the possibility of free electrons^{31,32} and holes contributing to the conductivity. This is not a lattice property but may be important in deducing the lattice conductivity from the measured values. We shall not consider this effect in this work except to remember that it may become important at the very highest temperatures; for example, near the melting point.

The use of Eq. (5) to obtain the total relaxation time can be questioned due to the nature of the N processes. These questions are considered in Appendix B and in

this work the relaxation times will be added reciprocally with τ_N considered simply another scattering mechanism.

III. THE CALLAWAY APPROXIMATION

Through various assumptions and approximations, Callaway⁵ has obtained the following integral expression for the thermal conductivity:

$$\kappa = CT^3 \int_0^{\theta_D/T} \frac{x^4 e^x (e^x - 1)^{-2} dx}{v_b/L + \alpha x^4 T^4 + (\beta_1 + \beta_2) x^2 T^5} + \kappa_2, \quad (6)$$

where

$$C = \left(\frac{k}{2\pi^2 v_s} \right) \left(\frac{k}{\hbar} \right)^3,$$

$\alpha = A (k/\hbar)^4$ —isotope scattering, $\beta_i = B_i (k/\hbar)^2$ —three-phonon scattering, $i=1$ (U process), $i=2$ (N process), θ_D = Debye temperature, κ_2 = a correction due to the conservative nature of N processes.³³ The assumptions needed to obtain this equation are as follows: (1) The sum over the phonon polarization has been set equal to three and an average phonon velocity v_s is used. (2) The τ_N^{-1} has been taken to be proportional to $T^3 \omega^2$, which is only valid for low-frequency longitudinal phonons.⁴ (3) τ_U^{-1} has also been taken to be proportional to $T^3 \omega^2$, a result which is neither a low-temperature nor a high-temperature approximation.³ (4) θ_D is usually taken to be the Debye temperature. While this is approximately the value of the longitudinal mode near the zone boundary, the transverse modes have a maximum of only one-third the Debye frequency for materials such as Ge and Si.¹⁶⁻¹⁸ (5) The relaxation times due to boundary scattering and impurity scattering are derived using average phonons for longitudinal and transverse branches.

These approximations would suggest that the Callaway equation pertains to longitudinal modes except that average velocities are used. Nevertheless, this equation has been used extensively, and successfully, to obtain values of κ versus T . The agreement found between this equation and experimental data on silicon and germanium using only $(B_1 + B_2)$ as an adjustable parameter indicates that it is a reasonable approximation for temperatures from 1°K to just above the maximum in κ .

One important result of the integral formulation is that it shows clearly that each of the scattering mechanisms are operative over a large temperature interval. The effect of varying the coefficients A and $(B_1 + B_2)$ can be seen from the calculations of Toxen⁸ and of Pohl,⁶ respectively. Increasing A lowers the conductivity symmetrically about the maximum. Increasing $B_1 + B_2$ decreases the entire high-temperature part of the curve

²⁶ P. Carruthers, Phys. Rev. **114**, 995 (1959).

²⁷ J. M. Ziman, Phil. Mag. **1**, 191 (1956).

²⁸ I. C. Pyle, Phil. Mag. **6**, 609 (1961).

²⁹ R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

³⁰ A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

³¹ B. I. Davydov and I. M. Shmushkevitch, Usp. Fiz. Nauk **24**, 21 (1940).

³² P. J. Price, Phil. Mag. **46**, 1252 (1955).

³³ This term is generally neglected in numerical calculations Toxen (Ref. 8) has indicated the strength of the term at low temperatures. This term will be discussed more fully in Appendix B.

from just below the maximum. An increase in the boundary scattering term has been shown¹² to decrease the curve from the lowest temperature to above the maximum. Thus, one cannot simply ascribe a temperature dependence in κ to a single scattering process.

A second result is that once the constants B_1+B_2 have been obtained for a material, the effects of impurities, boundaries, or any scattering mechanism operative at low temperatures can be investigated by simply varying the τ_b or τ_l term in a computer program. This approach has been used extensively.⁶⁻¹⁵

The Callaway equation appears to be a reasonable first step in obtaining qualitative fits to thermal conductivity data at low temperatures. However, the assumptions and approximations are such that it should not be used without some caution and without some regard for its limitations.

To explain the data above the Debye temperature, the high-temperature forms of the relaxation times are used in Eq. (4).

$$\tau_N^{-1} + \tau_U^{-1} = (D_1 + D_2)T\omega^2 = (\alpha_1 + \alpha_2)x^2T^3. \quad (7)$$

From Eqs. (4) and (7), and with $T > \theta_D$ and neglecting boundary scattering;

$$\kappa = \frac{C}{(\gamma_1 + \gamma_2)T} \frac{\theta_D \tan^{-1}u}{u}, \quad u = \frac{\theta_D}{T} \left(\frac{\alpha T}{\gamma_1 + \gamma_2} \right)^{1/2}. \quad (8)$$

The constants $D_1 + D_2$ can be related to the atomic mass, the Debye temperature and the Grüneisen constant.^{1,8,34} By using $D_1 \approx D_2$, Klemens has fit data on the lattice conductivity of copper-platinum alloys³⁵ and on germanium-silicon alloys.³⁶ This method has also been used successfully in several other cases.^{7,34,37,38}

There are, however, two important facts which indicate some inadequacies in the formulation at high temperatures: (1) The temperature dependence predicted by this theory is T^{-n} , $n \leq 1$, whereas in both silicon and germanium at temperatures from 200°K to well above the Debye temperature κ is found to vary as $T^{-1.2}$.^{39,40} This temperature dependence cannot be achieved with this formulation. (2) In general, the temperature region which has $\kappa \propto T^{-n}$ ($n \sim 1$) persists well below the Debye temperature; for example, from 200 to 1000°K in silicon ($\theta_D = 658$) and 150 to 950°K in germanium ($\theta_D = 372$). This formulation does not predict that the slope remain constant to such low temperatures.

One further point should be mentioned. In an equation of the form of (6), the upper limit is actually a

³⁴ B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, Phys. Rev. **125**, 44 (1962).

³⁵ P. G. Klemens, G. K. White, and R. J. Tainsh, Phil. Mag. **7**, 1323 (1962).

³⁶ P. G. Klemens, Westinghouse Research Report 929-8904-R3, 1961 (unpublished).

³⁷ J. E. Parrott, Proc. Phys. Soc. (London) **81**, 726 (1961).

³⁸ B. Abeles, Phys. Rev. **131**, 1906 (1963).

³⁹ G. A. Slack and C. Glassbrenner, Phys. Rev. **120**, 782 (1960).

⁴⁰ G. A. Slack and C. Glassbrenner (to be published).

frequency. If this equation correctly represents the thermal conductivity from low temperatures to above the maximum, it does so by indicating the behavior of the low-frequency phonons. This means that, at very high temperatures, Eq. (6) should still indicate the effects of the low-frequency phonons. However, Eq. (6), using the constants¹² which would give a fit to the silicon data at low temperatures, predicts a value of conductivity at the Debye temperature of about 14% of that measured. That is, the low-frequency phonons still carry part of the heat at the Debye temperature. This suggests that a sum of terms, for example, Eq. (6) plus Eq. (8) should be used to calculate κ correctly at high temperatures.

IV. NEW FORMULATION

Some of the objections pointed out in the last section are removed by taking into account the two types of polarization:

$$\kappa = \kappa_T + \kappa_L, \quad (9)$$

where

$$\kappa_T = \frac{2}{3} \int_0^{\theta_T/T} \frac{C_T T^3 x^4 e^x (e^x - 1)^{-2} dx}{\tau_T^{-1}}, \quad (9a)$$

$$\kappa_L = \frac{1}{3} \int_0^{\theta_L/T} \frac{C_L T^3 x^4 e^x (e^x - 1)^{-2} dx}{\tau_L^{-1}}, \quad (9b)$$

and

$$i = T, L; \quad x = \hbar\omega/kT; \quad \theta_i = k\omega_i/\hbar; \quad C_i = (k/2\pi^2 v_i)(k/\hbar)^3.$$

The subscripts T and L indicate transverse and longitudinal so that in C_T and C_L the appropriate v_T and v_L are used.

The relaxation times used are

$$\tau_T^{-1} = v_b/FL + A\omega^4 + B_T\omega T^4 + \tau_{TU}^{-1}, \quad (10)$$

$$\tau_{TU}^{-1} = B_T v \omega^2 / \sinh x, \quad \omega_1 < \omega < \omega_2, \quad (11)$$

$$\tau_{TU}^{-1} = 0, \quad \omega < \omega_1,$$

$$\tau_L^{-1} = v_b/FL + A\omega^4 + B_L\omega^2 T^3. \quad (12)$$

A is defined in Table I. The term κ_T can be again divided to give

$$\kappa = \kappa_{T0} + \kappa_{TU} + \kappa_L, \quad (13)$$

where

$$\kappa_{T0} = \frac{2}{3} T^3 \int_0^{\theta_1/T} \frac{C_T x^4 e^x (e^x - 1)^{-2} dx}{v_b/FL + \alpha x^4 T^4 + \beta_T x T^5}, \quad (13a)$$

$$\kappa_{TU} = \frac{2}{3} T^3 \int_{\theta_1/T}^{\theta_2/T} \frac{C_T x^4 e^x (e^x - 1)^{-2} dx}{v_b/FL + \alpha x^4 T^4 + \beta_{TU} x^2 T^2 / \sinh x}, \quad (13b)$$

$$\kappa_L = \frac{1}{3} T^3 \int_0^{\theta_3/T} \frac{C_L x^4 e^x (e^x - 1)^{-2} dx}{v_b/FL + \alpha x^4 T^4 + \beta_L x^2 T^5}, \quad (13c)$$

α and the β 's are defined as in Eq. (6). The N -process term $\beta_T x T^5$ was omitted from κ_{TU} . It is too small to

contribute at low temperatures and at high temperatures ($T > \theta_2$) it is expected to change to the form $\beta_T' \times T^2$ (see Table I). This is the same as the high-temperature form of τ_{TV} so that it contributes nothing new to the analysis. A better expression for τ_{TN} which would cover the transition from the low- to the high-temperature form would be very useful.

The first term in Eq. (13) is the contribution of the low-frequency transverse modes, $\omega < \omega_1$. The second term arises from the transverse modes with frequencies between ω_1 and ω_2 . The frequency at which the U processes start is ω_1 and ω_2 is the highest transverse mode frequency. The third term represents the longitudinal phonons.

The C_1 have been kept inside the integral in order to account for changes in the phonon velocities arising from the change in the density of phonon states as the frequency increases. This is important only for Eq. (13b). What we have assumed is that the velocity is constant at low frequencies and decreases abruptly at ω_1 . It remains constant between ω_1 and ω_2 and becomes zero above ω_2 . This is a reasonable approximation to the phonon spectrum¹⁶⁻¹⁸ (see Fig. 1). However, merely changing v in C_T will not necessarily take into account the density of phonon states correctly. The dependence of C_T on the velocity is obtained from three terms. The Boltzmann equation will give v^2 as in Eqs. (1) and (2), and the transformation to ω coordinates gives $dq = v^{-1}d\omega$. These velocities can be changed at ω_1 without difficulty. The density term $f(q, \lambda)$ in Eq. (3) gives a factor of v^{-2} at low frequencies, but is the troublesome term above ω_1 . It is possible to fit $f(q, \lambda)$ to an ω^2 law between ω_1 and ω_2 ,⁴¹ but the constant of proportionality will not be exactly v^{-2} . Thus, the velocity in $C_T(\omega > \omega_1)$ should be $v(\omega > \omega_1)/\bar{v}^2$ where \bar{v}^2 is an average velocity which actually allows you to count states correctly. We have simply used $[v(\omega > \omega_1)]^{-1}$ in C_T in Eq. (13b). The error from this approximation can be considered a multiplicative constant in C_T . However, the results indicate that Eq. (13b) is sensitive to only C_T/β_{TV} [see Eq. (17b)] at high temperatures and the total fit is not very sensitive to C_T at low temperature. Thus, this error in C_T does not significantly alter the results.

There are a number of further assumptions implicit in these equations. One concerns the use of single-mode relaxation times and the absence of any terms representing effects of N processes on other scattering processes. This is discussed in Appendix B. Another is the neglect of τ_{LU} , the U processes for the longitudinal modes, and all other possible scattering processes. A third concerns the form of the boundary scattering and impurity scattering terms. The velocities which appear in both τ_b and τ_I are average values, each a somewhat different type of average. It would be possible to use v_i , $i = T, L$ for the velocities in all cases, but this, in a sense, ignores the fact that scattering can take place

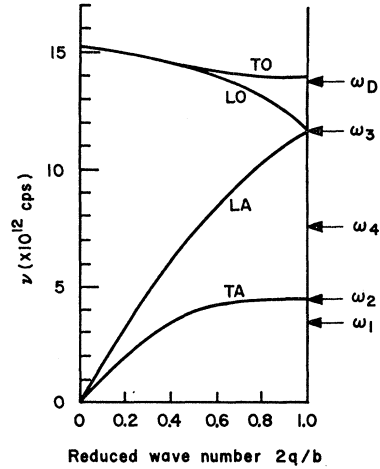


FIG. 1. Phonon spectrum for silicon after B. N. Brockhouse, Ref. 17.

from one mode to another. Thus, for lack of a better approximation, the same average value of v_s is used in both relaxation times. The value used is

$$v_b^{-1} = v_s^{-1} = \frac{1}{3}[2v_T^{-1} + v_L^{-1}]. \quad (14)$$

The reason this form is used will be indicated in Sec. V, but for the case of silicon and germanium all the various averages (averaging second or third powers) gives approximately the same value of v_s .

V. COMPARISON OF THE FORMULATIONS: AN ANALYSIS OF GERMANIUM AND SILICON

These equations can be integrated in the limits of high and low temperature, and their limiting forms are useful in obtaining numerical results. In the limit of low temperature (i.e., below 4°K) the new formulation can be expressed

$$\kappa \approx (4/15)\pi^4 \left\{ \frac{2}{3}C_T + \frac{1}{3}C_L \right\} \tau_b \{ 1 - 16\pi^4 \alpha T^4 \}, \quad (15)$$

where β_T and β_L terms have been neglected. The κ_{TV} term is negligible here. This expression is the same as the low-temperature limit of the Callaway equation⁵ if we substitute

$$\frac{2}{3}C_T + \frac{1}{3}C_L = C. \quad (16)$$

This implies that the v_s used in calculating C in the Callaway equation should be obtained as in Eq. (14).

At low enough temperatures, the α term is negligible and the boundary scattering can be checked. In many cases, the τ_b term is adjusted slightly to give a good fit at the lowest temperature.

At temperatures well above the Debye temperature where impurity scattering is small the new formulation can be expressed.

$$\kappa = \kappa_{T0} + \kappa_{TV} + \kappa_L, \quad (17)$$

$$\kappa_{T0} \approx \frac{2}{3}C_T [\theta_1^2 / (2\beta_T) T^4], \quad (17a)$$

⁴¹ Using the density function given by Phillips (Ref. 19).

TABLE II. Parameters used in the analysis.

	Silicon	Germanium	Comments
	(cm/sec)	(cm/sec)	
v_T	5.86×10^6	3.55×10^6	(a)
v_L	8.48×10^6	4.92×10^6	(a)
v_s	6.4×10^6	3.9×10^6	Eq. (17)
$v_T(\omega > \omega_1)$	2.0×10^6	1.3×10^6	(b)
$v_L(\omega > \omega_4)$	4.24×10^6	2.46×10^6	(b)
L	0.716 cm	0.24 cm	(c)
	(sec ⁻¹)	(sec ⁻¹)	
τ_b^{-1} (theory)	0.895×10^6	1.64×10^6	
τ_b^{-1} (exp)	1.16×10^6	1.96×10^6	$F \sim 0.8$ (d)
	(°K)	(°K)	
θ_1	180	101	(b)
θ_2	210	118	(b)
θ_3	570	333	(b)
θ_4	350	192	(b)
θ_D	658	376	(b)
Γ	2.16×10^{-4}	5.72×10^{-4}	
A	1.32×10^{-44} sec ³	2.40×10^{-44} sec ³	
$B_1 + B_2$	3.8×10^{-24} sec deg ⁻³	2.8×10^{-23} sec deg ⁻³	Eq. (6)
$D_1 + D_2$	3.1×10^{-19} sec deg ⁻¹	5.8×10^{-19} sec deg ⁻¹	Eq. (8)
B_T	9.3×10^{-13} deg ⁻³	1.0×10^{-11} deg ⁻³	
B_{TU}	5.5×10^{-18} sec	5.0×10^{-18} sec	
B_L	2.0×10^{-24} sec deg ⁻³	6.9×10^{-24} sec deg ⁻³	

^a From elastic constants of H. J. McSkimin, J. Appl. Phys. 24, 988 (1956).
^b Silicon values from Ref. 17; germanium values from Ref. 16.
^c The germanium sample was actually larger than this, but contained several grain boundaries. This value of L was obtained by comparison to several other smaller samples which had the same conductivity at 4.2°K.
^d A value of $F = 0.8$ would be predicted from the width to length ratio of the samples. See Refs. 24 and 25.

$$\kappa_{TU} \approx \frac{2}{3} \left(\frac{C_T'}{\beta_{TU}} \right) \frac{1}{T} \left\{ \frac{\theta_2^2 - \theta_1^2}{2} - \frac{1}{5} \frac{\alpha}{\beta_{TU}} \frac{\theta_2^5 - \theta_1^5}{T} \right\}, \quad (17b)$$

$$\kappa_L \approx \frac{1}{3} C_L (\theta_3 / \beta_L T^3), \quad (17c)$$

C_T' is C_T calculated using v_T ($\omega_T > \omega_1$).

The expansion of Eq. (8) at the same temperature gives

$$\kappa = \frac{C}{(\gamma_1 + \gamma_2) T} \left[\theta_D - \frac{1}{3} \frac{\theta_D}{T} \left(\frac{\alpha}{\gamma_1 + \gamma_2} \right) \right]. \quad (18)$$

At this temperature, κ_{T0} is usually negligible and κ_L is only a few percent. Thus, κ_{TU} dominates and gives a T^{-1} temperature dependence if the α term is small. Equation (18) also gives a T^{-1} temperature dependence, if the α term is again small, but there are three important differences: (1) The Debye temperature θ_D is not the important parameter in κ_{TU} and (2) as the temperature decreases κ_{TU} eventually becomes very small. There is no such cutoff provision in Eq. (8). (3) Since κ_L increases as T decreases, the temperature dependence of the total κ 's in Eq. (17) is greater than T^{-1} .

The parameters used in the analysis are listed in Table II. The B's and D's are obtained from the curve fitting and τ_b is also adjusted to fit the low-temperature data. (The τ_b obtained experimentally is actually very close to that obtained using the length to width

correction.^{24,25}) Figure 1 shows the phonon spectrum of silicon¹⁸ and indicates the position of the frequencies used in the analysis. The germanium spectrum is very similar. The values of ω_1 were obtained by assuming that the phonon spectrum is isotropic.^{17,19} The actual anisotropy certainly could alter these frequencies slightly. This would also alter the values of v_i obtained near ω_1 and ω_4 . The results are fairly insensitive to variations in ω_3 and ω_4 .

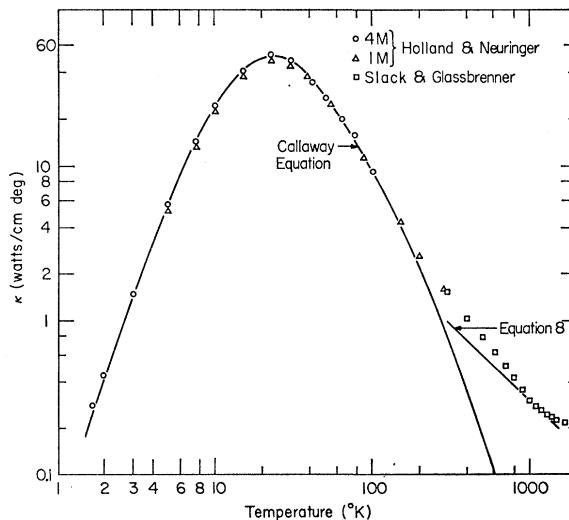


FIG. 2. Thermal conductivity of silicon.

A fit of the data on high purity silicon using the Callaway equation is shown in Fig. 2. The experimental data are taken from Holland and Neuringer⁴² (1.7 to 300°K), and Slack and Glassbrenner⁴⁰ (300 to 1683°K). The two sets of data agree within two percent at room temperature. A fit at high temperature, obtained from Eq. (8), is also shown. The value of $(D_1 + D_2)$ is obtained from the 1000°K data using Eq. (18).

In Fig. 3, the same silicon data are fit using the new formulation. Each contribution is shown. The value of κ_{TV} is obtained from the 1000°K data using Eq. (17b). κ_L is then obtained from the data near room temperature with the value of κ_{TV} taken into account. κ_{T0} will be insignificant at 300°K. κ_{T0} is then obtained from the best fit for the low-temperature data with κ_{TV} and κ_L taken into account. This procedure may seem somewhat arbitrary but the important point is that the data can not be fitted over the complete range 1.5 to 1300°K if

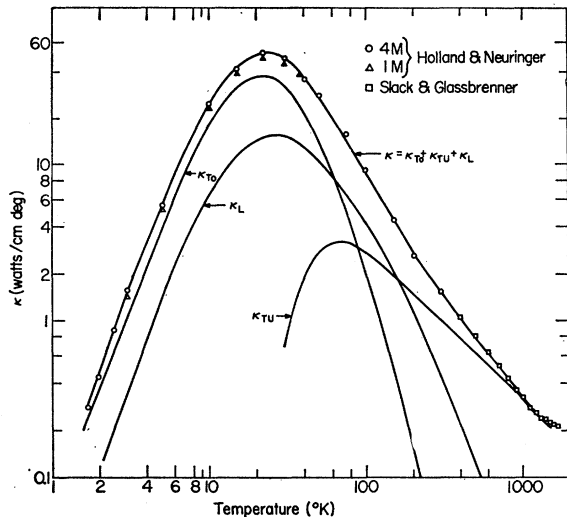


FIG. 3. Thermal conductivity of silicon. Solid lines are the new analysis.

any one of the three terms is omitted, even if the constants C , α , and β are all varied. (C and α should only be varied by changing ν_i so that they were not changed by more than an order of magnitude.)

In Fig. 4 the new analysis is used to fit data on germanium. The experimental data are taken from Slack and Glassbrenner^{39,40} (200 to 900°K) and Holland⁴² (1.7 to 200°K). The value of κ_{TV} is obtained from the 700°K data; τ_b is adjusted to fit the data at 2°K and κ_{T0} and κ_L are obtained as for silicon.

From Figs. 3 and 4, it is obvious that the agreement is excellent over a very large temperature range. In both cases, the poorest fit occurs in the region in which κ_{TV} has its maximum as might be expected since the values here are highly sensitive to ω_1 which is one of the least accurately determined parameters.

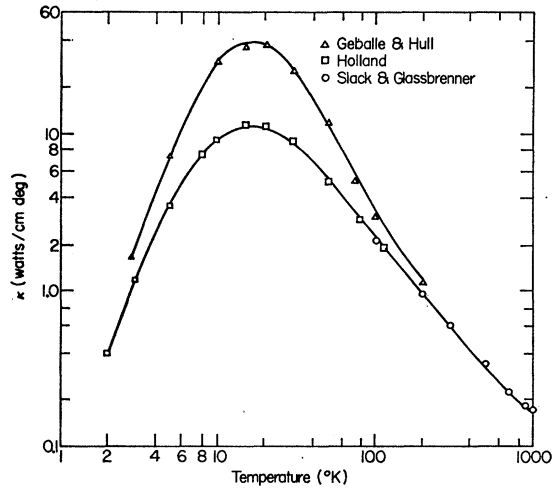


FIG. 4. Thermal conductivity of germanium. Solid lines are the new analysis.

At high temperatures the analysis predicts the change in slope found in the experimental data near 1000°K for silicon and near 700°K for germanium. It has previously been suggested³⁹ that this is due to the onset of an electronic contribution to the thermal conductivity. The present work suggests that it is in part due to the dying out of the longitudinal mode contribution.

It appears possible to fit data on various materials even if the high-temperature results are not available. For example, for germanium, it was found that κ_L is insensitive to the choice of B_L for $T < 20^\circ\text{K}$. Thus, once τ_b is determined from Eq. (15), a value of B_T can be chosen to make the curve fit up to 20°K. Since κ_{TV} does not become important till about 40°K, the value of B_L can be chosen to make $\kappa_{T0} + \kappa_L$ fit the data up to 40°K. Then B_{TV} can be picked so that the curve can be fitted up to higher temperatures. This approach is not expected to give as good a fit.

As a further check on this new analysis the data on isotropically pure germanium were fitted. The value of Γ was calculated from the isotropic constituents given by Geballe and Hull⁴³ and a value of $\Gamma_{Is} = 3.68 \times 10^{-5}$ was obtained. Since this value of Γ is about 15 times less than that for normal germanium, the value of α was decreased by that factor; all other constants remaining unchanged. The fit is shown in Fig. 4. τ_b was adjusted slightly to improve the low-temperature fit.

The fit is very good below 50°K but the experimental points are lower than the theoretical curve above 50°; the range in which three-phonon scattering is important. It is quite possible that the phonon frequencies ω_1 and ω_2 are influenced by the absence of isotopes in the material. This effect is expected to be small, varying about as $\bar{M}^{-1/2}$ where \bar{M} is the average mass.⁴⁴ It is also possible that the perturbation of the frequency spec-

⁴³ T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

⁴⁴ A. A. Maradudin, G. H. Weiss, and D. W. Jepsen, J. Math. Phys. **2**, 349 (1961).

⁴² M. G. Holland, Bull. Am. Phys. Soc. **8**, 15 (1963).

trum will cause a variation in the strength of the three-phonon processes and the indication from these results is that the relaxation times should be increased slightly in isotropically pure material. This result was also noted by Toxen⁸ and Abeles *et al.*³³ for the germanium-silicon alloys. This effect has been calculated by Carruthers.⁴⁵

In order to check the range in which the new formulation and the Callaway equation agree, the impurity scattering parameter α was increased by a factor of 3 in both Eqs. (6) and (13). The results for silicon are shown in Fig. 5. This indicates that the Callaway equation is quite adequate for examining impurity effects to temperature somewhat above the maximum as long as there is not too much significance attached to the parameter (B_1+B_2).

VI. CONCLUSIONS

We feel that the importance of this work lies in the attempt to use the known phonon spectrum in order to divide the heat flow into that due to longitudinal and transverse phonons. There are several adjustable parameters in these equations so that the analysis is, to some extent, phenomenological. However, we have *not* found it possible to fit the high-temperature data with only one integral and the use of two or more integrals cannot be justified without considering two-mode conduction.

Germanium and silicon have proved to be of great use in this work because of their very dispersive phonon spectra. Without this the simple expression for τ_{TV} could not have been obtained and the excellent fits could not have been made over such a large range of temperature.

For materials which do not have a transverse phonon branch with as much dispersion as silicon or germanium, one expects that the form of τ_{TV} would not be accurate over the complete temperature range. In this case the analysis near and above the maximum must be handled more carefully. However, one would still expect that U processes should die out at low enough frequencies so that a separation into three equations should have some validity.

The high-temperature expression for τ_{TV} is still expected to hold. Now, however, there is provision for the temperature dependence of the thermal conductivity to be greater than or less than T^{-1} since this will depend on the relative number and the relative scattering probabilities of longitudinal and transverse modes.

There are cases in the literature in which the type of analysis presented here might explain apparent difficulties. Callaway and von Baeyer,⁷ in attempting to fit the data on isotope scattering in LiF, found it necessary to include an exponential dependence in τ_U^{-1} to fit the results between 55 and 80°K, well above the maximum. However, this exponential is inconsistent with the value of τ_U^{-1} needed to fit the data near the

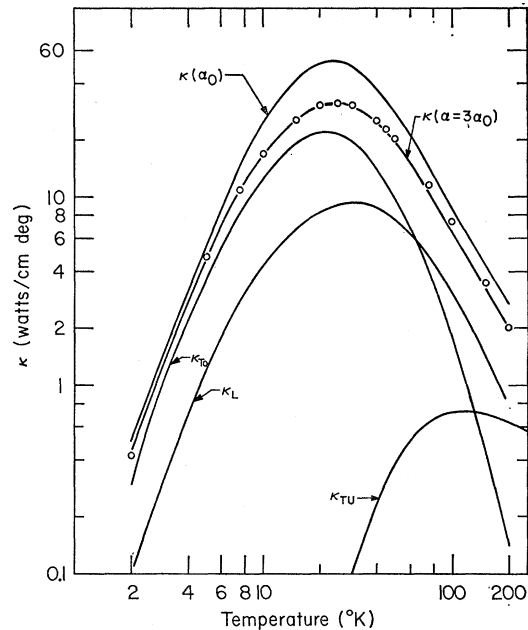


FIG. 5. The effect of increased impurity scattering on the analysis of the thermal conductivity of silicon. The circles are from the Callaway equation.

maximum. A formulation of the type presented here would eliminate this problem since the κ_{TV} term, which contains the exponential, would not contribute much near the maximum.

Parrott,³⁶ after attempting to fit high-temperature data on germanium-silicon alloys, has concluded that the high-temperature heat flow is due primarily to transverse phonons. This result is also predicted by our approach.

The analysis presented here has the advantage that it is, in principle, a simple extension of existing theories and that it is physically quite plausible. There are several other possibilities that might be considered for lattice conduction, depending on the materials studied. Some of these are: (1) U processes for the high-frequency longitudinal modes,¹ (2) optical-mode conduction and scattering at high temperatures,³⁷ and (3) the addition of four-phonon processes at high temperatures.^{39,46} There are also the questions of the validity of the single-mode relaxation times, the need for terms representing the influence of N processes on the other scattering times and scattering between modes. However, it appears that two-mode conduction is a more important consideration.

At low temperatures in the Debye region, two-mode conduction can be adequately represented by considering one average phonon. Thus, in the impurity scattering and boundary scattering regions, this analysis and the Callaway analysis give essentially the same results so that the simpler Callaway form is quite useful in studying impurity and boundary effects.

⁴⁵ P. Carruthers, Phys. Rev. **126**, 1448 (1962).

⁴⁶ I. Pomeranchuk, J. Phys. (USSR) **7**, 197 (1943).

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 APPENDIX A: UMKLAPP-PROCESS
RELAXATION TIME

In a general approach to the relaxation time due to U processes, Klemens^{1,3} has obtained an expression which can be written

$$\tau_U^{-1} = - \sum_{q'q''} A_{qq'q''} \frac{\lambda \cdot \mathbf{b}}{\lambda \cdot \mathbf{q}} \frac{(e^x - 1)}{(e^{x'} - 1)(e^x - e^{-x'})}, \quad (\text{A1})$$

subject to

$$\Delta\omega = \omega + \omega' + \omega'' = 0 \quad (\text{A2})$$

$$\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = \mathbf{b}, \quad (\text{A3})$$

and where

$$A_{qq'q''} \propto \omega\omega'\omega''.$$

Since $\lambda \cdot \mathbf{b} < 0$ and $\lambda \cdot \mathbf{q}$ is proportional to ω we have

$$\tau_U^{-1} \propto \sum_{q'q''} \omega'\omega'' \frac{(e^x - 1)}{(e^{x'} - 1)(e^x - e^{-x'})}.$$

We first consider the interaction $T+T \rightarrow L$, that is, (ω, q) and (ω', q') are transverse (T) modes and (ω'', q'') is a longitudinal (L) mode. We then obtain, by changing the sum to a surface integral in ω space and recalling condition (A2),

$$\tau_{TU}^{-1} \propto \int \omega'\omega'' \frac{e^x - 1}{(e^{x'} - 1)(e^x - e^{-x'})} \frac{dS'}{\nabla_q(\Delta\omega)}. \quad (\text{A4})$$

If now we examine Fig. 6, the phonon spectrum for a

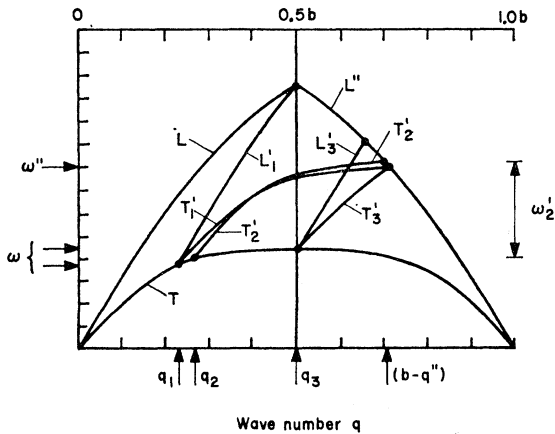


FIG. 6. Phonon spectrum showing the zone boundary (0.5b) and the extension into the second zone.

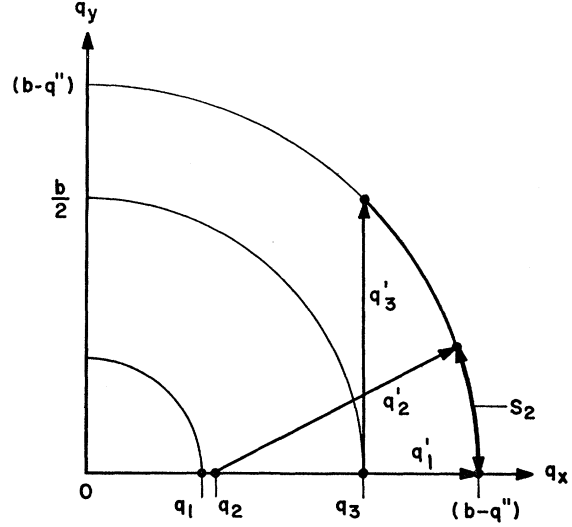


FIG. 7. Phonon spectrum showing construction needed to provide the interacting surface.

material such as silicon or germanium,^{16,17} we see that $\omega' \sim \omega$ and since $\Delta\omega = 0$, $\omega'' \sim 2\omega$. [$-\omega(-q) = \omega(+q)$ in the usual normal mode notation.] Thus, we have

$$\tau_{TU}^{-1} \propto \frac{\omega^2}{(e^x - e^{-x})} \int \frac{dS'}{\nabla_q \Delta\omega}. \quad (\text{A5})$$

The surface integral can be obtained from geometrical considerations. Since $\omega \sim \omega' = \omega''/2$ and since transverse modes, which are interacting, are on the flat section of the dispersion curves we can represent the q 's as shown on Fig. 7.

The surface is then of the form,

$$S \sim \left[3\pi b \Delta \left(1 - \frac{\Delta}{b} \right) / \left(1 + \frac{4\Delta}{b} \right) \right], \quad (\text{A6})$$

where we have approximated $(b - q'') \sim \frac{3}{4}b$, and $q = (b/4) + \Delta$. This shows that $S = 0$ for $q \sim b/4$, or $\omega = \omega_1$. From Fig. 7 it is clear that once q is slightly larger than $q_1 (\sim b/4)$ the surface area increases quickly. Thus, there will be a frequency dependence in S near $q_1(\omega_1)$ but it will be very weak as soon as q is slightly larger than q_1 . This frequency dependence will be neglected here.

The $\nabla_q(\Delta\omega)$ will be approximately v_L (at ω'') so that the form of τ_{TU}^{-1} is as given in Table I.

The interaction $T+L \rightarrow L$ should also be considered. This interaction might be expected to give U processes for all the transverse mode frequencies. However, for germanium and silicon it is found that these processes would also not begin until $\omega > \omega_1$. At

higher frequencies the strength of this term will be less than the $T+T \rightarrow L$ term by a factor of e^{-10}/e^4 . Since all other terms in the scattering probability are about the same, this term is neglected.

The form of τ_{TU}^{-1} is still an approximation in the sense that the frequency dependence is not clear cut; however, it is a reasonable approximation.

In a physical sense, a relaxation time of the form $\tau_N^{-1} = B\omega^2 T^3$ used in the text for longitudinal modes, may already take U processes into account. N processes of the form $L+T \rightarrow L$ will change low-frequency longitudinal phonons to high-frequency longitudinal phonons. It is only these high-frequency longitudinal phonons which can U scatter. Now, if the scattering probability is very large for these high-frequency phonons to umklapp scatter they will not remain in this high-frequency state very long. However, the limiting process which will determine the umklapp relaxation time will be of the form $\omega^2 T^3$ which describes the occupancy of the high-frequency state from which the phonon is scattered.

To see the inadequacy of an umklapp scattering time of the form $B\omega^2 T^3$, we look at Eq. (A4). Klemens,³ in deriving τ_U^{-1} , used the conditions

$$|\omega| + |\omega'| + |\omega''| \sim \omega_D, \quad (\text{A7})$$

$$\omega \ll \omega' \sim \omega'' \sim \omega_D. \quad (\text{A8})$$

He then made the approximations $x \ll 1$ and $x' \gg 1$ in Eq. (A4) and obtained

$$\tau_U^{-1} \sim \omega^2 T^3 \int x'^3 e^{-x'} dx, \quad (\text{A9})$$

$$\tau_U^{-1} \propto \omega^2 T^3 e^{-\theta/\alpha T}, \quad (\text{A10})$$

where α depends on the limits of integration which in turn depend on the phonon spectrum. If αT is very small with respect to $\hbar\omega'$, the exponential should appear in τ_U . However, if αT is large with respect to $\hbar\omega'$, the results would be

$$\tau_U^{-1} \propto \omega^2 T \theta_D^2, \quad (\text{A11})$$

which is the typical high-temperature form of τ_U^{-1} .

APPENDIX B: TOTAL RELAXATION TIME

N processes play a special role in thermal conduction since they are the only momentum-conserving scattering processes. N processes cannot cause thermal resistance in themselves, but can transfer momentum from one part of the frequency distribution to another thereby influencing the other scattering processes. Because of this coupling, it may be expected that the addition of reciprocal relaxation times is not a good approximation. Klemens has shown that in the presence of N processes, the total relaxation time can be ex-

pressed^{1,3}

$$\tau(\omega) = \frac{\tau'(\omega)[\tau_N(\omega) + \lambda(\omega)]}{\tau'(\omega) + \tau_N(\omega)}, \quad (\text{B1})$$

where $\tau_N(\omega)$ is the (single-mode) relaxation time due to N processes, $\tau'(\omega)$ is the relaxation time due to all other processes and $\lambda(\omega)$ is an appropriate average value of $\tau(\omega')$ for the modes ω' which are linked to mode ω by N processes. Klemens,^{35,36} indicates that the term $\tau'\lambda/(\tau' + \tau_N)$ can be neglected in general, unless point-defect scattering is weak compared to U processes, but in this case N processes turn out to be unimportant.

Callaway, on the other hand, obtained an integral expression for λ (β in Ref. 5) by assuming it independent of ω . In this way, he obtains a correction term for the thermal conductivity

$$\kappa = \kappa_1 + \kappa_2, \quad (\text{B2})$$

where κ_1 is Eq. (6), and

$$\kappa_2 = C(I_2^2/I_3), \quad (\text{B3})$$

with

$$I_2 = \int_0^{\theta'/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (\text{B4})$$

$$I_3 = \int_0^{\theta'/T} \frac{\tau_c}{\tau_N} \left(\frac{1}{\tau_c} - \frac{1}{\tau_N} \right) \frac{x^4 e^x}{(e^x - 1)} dx. \quad (\text{B5})$$

Now consider the situation T very high, θ' very low. That is, the high-temperature contribution of the low-frequency modes ($\omega < \omega' = k\theta'/\hbar$). If θ' is low enough, one expects the conservation conditions will not allow U processes for the frequencies $\omega < \omega'$. In this case we obtain

$$\kappa_2 = C \frac{\beta_2}{\alpha} \left[\int_0^{\theta'/T} \frac{x^2 dx}{\alpha x^2 + \beta_2 T} \right]^2 \bigg/ \left[\int_0^{\theta'/T} \frac{x^6 dx}{\alpha x^2 + \beta_2 T} \right]. \quad (\text{B6})$$

Where the terms are defined in Eq. (6) and β_2 is for N processes alone. (Callaway's $B_1 = 0$). Solving this we obtain

$\kappa_2 =$

$$\left[\frac{C\theta'}{\beta_2 T^3} \frac{1}{u^4} \left(1 - \frac{\tan^{-1} u}{u} \right)^2 \right] \bigg/ \left[\frac{1}{5} - \frac{1}{3} \frac{1}{u^2} + \frac{1}{u^4} \left(1 - \frac{\tan^{-1} u}{u} \right) \right],$$

where $u = (\theta'/T) (\alpha/\beta_2 T)^{1/2}$. When u is small this becomes

$$\kappa_2 = \left(\frac{C}{\beta_2} \right) \left(\frac{\theta'}{T^3} \right) \frac{7}{9} u^{-2} \left(1 - \frac{3}{5} u^2 \right)^2. \quad (\text{B8})$$

Thus, this term becomes very large due to u^{-2} . If we use values of α , β , and C consistent with the low-temperature fits on silicon,¹² and take $\theta' \sim 200^\circ$, this term is several orders of magnitude higher than the measured conductivity at $T \sim 500^\circ \text{K}$.

Physically this means that even when there is no divergence in the calculated κ at low temperatures due to a lack of U processes (boundary scattering will make the integrals converge) the low-frequency modes would cause extremely high conductivity at high temperature. Thus, we deduce either κ_2 does not properly take the coupling of N processes into account or the value τ_N^{-1} used in this work does not represent solely N pro-

cesses for the longitudinal modes (as indicated at the end of Appendix A).

For the case of the transverse modes we have indicated $\tau_U^{-1} \gg \tau_N^{-1}$ at temperatures above the maximum, in this case κ_2 , would be negligible.

These considerations lead us to use the Klemens approach in which Eq. (B1) reduces to Eq. (5) and N processes are simply an added scattering mechanism.

Diffusion of Palladium in Copper and Silver*

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The diffusion of palladium in single crystals of copper and silver has been measured by the tracer-sectioning technique. The results are

$$D_{\text{Pd-Cu}} = 1.71_{-0.21}^{+0.23} \exp[-(54\,370 \pm 300)/RT] \text{ cm}^2/\text{sec},$$

and

$$D_{\text{Pd-Ag}} = 9.57_{-1.37}^{+1.63} \exp[-56\,750 \pm 300)/RT] \text{ cm}^2/\text{sec}.$$

The difference between the activation energies for Pd diffusion and self-diffusion in copper and silver is in only qualitative agreement with the theories of Lazarus and LeClaire. Correlation factors for palladium diffusion in silver are calculated using Lidiard's theory and the data on silver diffusion in palladium-silver alloys by Nachtrieb *et al.* From these correlation factors and Manning's theory, it is shown that palladium atoms repel vacancies in silver. This is in disagreement with the quenching studies of Hamaguchi.

INTRODUCTION

IT has been shown experimentally that activation energies for the diffusion of impurities at near-zero concentration in a given solvent may be considerably different from the activation energy for self-diffusion of the solvent. In 1954, Lazarus¹ proposed a theory of impurity diffusion based on the electrostatic interactions between the impurity ion and the neighboring vacancy and solvent atoms. This model was based on the picture of an impurity of charge Z dissolved in a metal and screened by the conduction electrons. The resulting potential distribution around the impurity was assumed to be described by the linearized form of the Thomas-Fermi equation. The change in energy of vacancy formation was considered to be the change in the lattice binding energy of a nearest neighbor in the screened potential of the impurity atom. The change in the energy of motion was viewed as a corresponding change in the appropriate elastic constants. This theory predicted that the activation energy for impurity diffusion should be less than solvent self-diffusion for electropositive impurities and greater for electronegative impurities.

Although fair agreement between theory and experiment was found for electropositive impurities diffusing

in copper and silver,² for electronegative impurities (iron, cobalt, and nickel in copper,³ ruthenium in silver,⁴ and platinum in gold⁵) only the sign of the activation energy difference was predicted correctly.

An alternative theoretical derivation of the difference, ΔQ , between the activation energies for impurity diffusion and solvent self-diffusion has recently been proposed by LeClaire.⁶ The change in energy of vacancy formation was calculated in the same manner as in the Lazarus treatment, but the change in energy of motion was considered to be the difference in electrostatic energy between the configuration corresponding to the impurity atom at the saddle point and that with the impurity at the equilibrium lattice position. LeClaire used the more accurate numerical solution of the Thomas-Fermi equation as calculated by Alfred and March,⁷ and also took into account the temperature dependence of the correlation factor, f , for impurity diffusion.

LeClaire's theory provided improved agreement with experiment for the electropositive impurities, although

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