Temperature Dependence of Three-Phonon Processes in Solids, with Application to Si, Ge, GaAs, and InSb

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The temperature dependence of three-phonon processes in solids is discussed in terms of the exponent m in relations of the type $\tau \propto T^{-m}$ where the value m is given by $m = -T\tau^{-1}d\tau/dT$. A method is given for placing bounds on the value of m for three-phonon processes involving various energies of phonons at any given temperature. Application to Si, Ge, GaAs, and InSb shows considerable similarity in the temperature dependences of the three-phonon relaxation times of longitudinal and transverse phonons. This similarity is most noticeable at the higher temperatures.

I. INTRODUCTION

HE relaxation of phonons via three-phonon processes has often been represented mathematically by expressions of the type $\tau^{-1} \propto g(\omega) T^m$ or $\tau^{-1} \propto \omega^p T^m$. At very high temperatures $(T \gg \Theta_D)$, it is currently accepted¹ that $\tau^{-1} \propto T^1$ for all types of phonons if only three-phonon relaxation processes are considered. At very low temperatures, Herring² has shown that expressions of the type $\tau^{-1} \propto \omega^p T^m$ are quite appropriate for three-phonon relaxation processes and has deduced the proper values of p and m for various phonon polarizations and crystal types. In the intermediate temperature ranges, it is convenient to describe the three-phonon relaxation times by expressions of the type $\tau^{-1} \propto g(\omega) f(T)$. Then it is possible to judge the propriety of the particular function f(T) by replacing it at any given temperature T by $A_T T^m$. One may ascertain the required value of m and judge the credibility of that value. The function f(T) will be well represented by the function $A_T T^m$ over a short range of temperature about the temperature T, if one chooses fixed values of A_T and m in such a way as to match both the algebraic values and temperature derivatives of the two functions at the temperature in question. When this is done, the value of m is given by

$$m = T f^{-1} df / dT, \qquad (1)$$

and under these circumstances, we shall say that $f(T) \propto T^m$ at the particular temperature.

Descriptions of the type just indicated are convenient for relaxation times because of the possible comparisons both with Herring expressions² and with the known high-temperature dependence first suggested by Peierls.¹ Such descriptions are also convenient because it is possible to put bounds on the values of m if one knows certain minimal information about the phonon spectrum.

II. DERIVATION OF THE BOUNDS FOR THE THE TEMPERATURE EXPONENT IN THE RELAXATION-TIME PROPORTIONALITY

We wish to set limits of the type $\tau^{-1} \propto T^m$, $m_1 < m < m_2$, for three-phonon relaxations for various types of polarizations of phonons at particular temperatures in certain chosen solids of interest. These limits will be based on the energy region occupied by the particular polarization and on the energies of the other phonons interacting in the three-phonon processes. In order to derive these limitations on m, we must first point out some properties of the values of exponents which become apparent during the addition of functions.

Theorem I. At any given temperature T, if $f_1(T) \propto T^{n_1}$ and $f_2(T) \propto T^{n_2}$, then at the same temperature, the sum function, $f = f_1 + f_2$, has the property that $f(T) \propto T^n$, where n is given by $n = (n_1 f_1 + n_2 f_2)(f_1 + f_2)^{-1}$.

Since the proof is readily obtained by direct application of the definition of Eq. (1), we shall not present it.

The following corollary of Theorem I is the cornerstone of the present article.

Corollary I. At any given temperature T, if $f_1(T)$ and $f_2(T)$ are positive functions where $f_1(T) \propto T^{n_1}$ and $f_2(T) \propto T^{n_2}$ where $n_1 < n_2$, and if a and b are positive constants, then the sum function $f = af_1 + bf_2$ has the property that $f \propto T^n$, where $n_1 < n < n_2$.

The validity of the preceding corollary is fairly obvious if one notes that af(T) has the same temperature exponent as f(T) and if one then regards the operation in Theorem I as being that of computing a weighted average.

Corollary I is useful at higher temperatures, where isotope and boundary scattering may be ignored, because τ^{-1} is then additively composed of three-phonon events whose temperature exponent can be calculated. This is under the assumption that we may ignore higher order phonon events.

Corollary II. If $f_1(T)$ and $f_2(T)$ are positive functions, where $f_1 \propto T^{n_1}$ and $f_2 \propto T^{n_2}$, then the difference function $f = (f_1 - f_2)$ has the property that $f \propto T^n$, where $n = (n_1 f_1 - n_2 f_2)(f_1 - f_2)^{-1}$.

¹ R. Peierls, Ann. Physik 3, 1055 (1929).

² C. Herring, Phys. Rev. 95, 954 (1954).

In order to derive the temperature dependence of the three-phonon relaxation times, we must first define the relaxation times. We shall adhere fairly closely to the thermal conductivity method of Callaway.3,4 In this method, two types of scattering events are recognized, yielding two types of relaxation time, τ_N and τ_R , where quasimomentum is conserved by the first type of relaxation event, but not by the second type of event, sometimes called an R process. The two types of relaxation time are defined by implication in Eq. (2) of Callaway's article on thermal conductivity. This equation is of the general form

$$\left(\frac{\partial N}{\partial t}\right)_{\text{coll}} = \frac{N(\lambda) - N}{\tau_N} + \frac{N_0 - N}{\tau_R}.$$
 (2)

In Eq. (2), given above, $N = N(\mathbf{q}, T)$ is the actual phonon occupation number, $N_0 = N_0(\mathbf{q},T)$ is the occupation number at equilibrium, with the temperature gradient removed, (i.e., a Planck distribution), and $N(\lambda) = N_{\lambda}(\mathbf{q},T)$ is the equilibrium toward which N processes tend and is of the form

$$N_{\lambda}(\mathbf{q},T) = \left[\exp\left(\frac{h_{\nu} - \lambda \cdot \mathbf{q}}{K_{B}T}\right) - 1 \right]^{-1}, \qquad (3)$$

hereinafter called a λ distribution.

Equation (2) implies that $(\partial N/\partial t)_{coll}$ is made up of two parts,

$$(\partial N/\partial t)_{\text{coll, }N \text{ type}}$$
, and $(\partial N/\partial t)_{\text{coll, }R \text{ type}}$,

where

and

$$(\partial N/\partial t)_{\text{coll, }N \text{ type}} = (N(\lambda) - N)/\tau_N$$
 (4)

$$(\partial N/\partial t)_{\text{coll, } R \text{ type}} = (N_0 - N)/\tau_R.$$
 (5)

We shall concern ourselves first with the N-process relaxation. If we let

$$n_{\lambda} = N(\mathbf{q},T) - N_{\lambda}(\mathbf{q},T),$$

$$-n_{\lambda}(\mathbf{q},T)\tau_{N}^{-1}(\mathbf{q},T) = \left[\frac{\partial N(\mathbf{q},T)}{\partial t}\right]_{\text{coll, }N \text{ type}}.$$
 (6)

We shall ignore phonon-phonon processes involving four or more phonons. We may find τ_N^{-1} for three-phonon processes by comparing Eq. (5) with the quantummechanical equations for $[\partial N(\mathbf{q},T)/\partial t]_{\text{coll, }3P, N \text{ type}}$. For this purpose we shall need to refer to the distinction between a three-phonon event of the form $P_{\text{heat carrier}}$ $+P_2 \rightarrow P_3$, and one of the splitting type, $P_{\text{heat carrier}} \rightarrow$

 $P_2 + P_3$. We shall call these processes events of class I and class II. When this distinction is maintained, one finds that the time rate of change of the phonon population number due to N-type three-phonon events is given, correct to the first power of the various n_{λ} , by the following:

$$\begin{pmatrix} \frac{\partial N}{\partial t} \\ \frac{\partial N}{\partial t} \end{pmatrix}_{\text{coll, } 3P, N \text{ type}}$$

$$= \sum_{\mathbf{q}', \mathbf{q}''; \text{ Class I events}} A_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} [-n_{\lambda}(N_{\lambda}'-N_{\lambda}'') \\ -n_{\lambda}'(N_{\lambda}-N_{\lambda}'')+n_{\lambda}''(N_{\lambda}'+N_{\lambda}+1)]$$

$$+ \sum_{\mathbf{q}', \mathbf{q}''; \text{ Class II events}} A_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} [-n_{\lambda}(N_{\lambda}'+N_{\lambda}''+1) \\ +n_{\lambda}'(N_{\lambda}''-N_{\lambda})+n_{\lambda}''(N_{\lambda}'-N_{\lambda})].$$
(7)

It is understood that the sums above are to include only those three-phonon events which conserve quasimomentum. The non-negative factors $A_{q,q',q''}$ are nearly independent of temperature over a wide temperature range. In obtaining Eq. (7), use has been made of the fact that N processes leave a λ distribution stationary, and this has removed the zero-order terms in the various n_{λ} . Equation (7) is easily derived from Eq. (6.6) of Klemens' article,⁵ provided one is careful to note Klemens' notational convention mentioned on page 26 of the same paper.

In order to proceed properly from Eq. (7) above, we need to know the relation between n_{λ} , n_{λ}' , and n_{λ}'' , so that n_{λ}' and n_{λ}'' may be replaced by some multiple of n_{λ} , following which we may calculate τ_N . This ratio of n_{λ}'/n_{λ} , etc., would probably be temperature and frequency-dependent, and we have no way of ascertaining its proper value in each case. Therefore we must settle for a "single-mode" relaxation time τ_N , setting n_{λ} and $n_{\lambda}^{\prime\prime}$ equal to zero. Following this, we see from Corollary I that the temperature dependence of τ_N^{-1} $\equiv -(1/n_{\lambda})(\partial N/\partial t)_{\text{coll, }3P, N \text{ type}}$ is bounded by the extremes of the temperature dependences of the various allowed $(N_{\lambda}' - N_{\lambda}'')$ and $(N_{\lambda}' + N_{\lambda}'' + 1)$, where temperature dependence refers to the value of the exponent in relations of the type obtained in Eq. (1).

For small thermal gradients, $\lambda \approx 0$ and the various N_{λ} may be replaced by N_0 in the bracket expressions above.

The contributions to τ_R^{-1} may be divided into that from boundary scattering, impurity scattering, and phonon-phonon scattering. Following common usage, we call the last named contributor to τ_R^{-1} , "umklapp scattering," and label its contribution with the symbol τ_u^{-1} . Once again, we shall ignore phonon-phononscattering events involving four or more phonons. Under these circumstances, a derivation similar to the one just detailed for τ_N^{-1} is readily available for τ_u^{-1} . It may be found in Klemens' review article, page 39.5 In

³ J. Callaway, Phys. Rev. 113, 1946 (1959). ⁴ Our notation differs slightly from that of J. Callaway. For the quantity which we call τ_R^{-1} , Callaway used τ_u^{-1} . We wish to reserve τ_u^{-1} for the inverse relaxation time due to nonmomentumconserving phonon-phonon scattering arising from anharmonicities in the lattice potential term. Callaway had no separate symbol for this.

⁵ P. G. Klemens, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

the τ_u derivation, it is convenient to define $N-N_0 \equiv n$. It is found possible to obtain a relation between the n, n', and n'' by assuming a λ distribution, so that the various n', and n'' need not be arbitrarily set equal to zero in the equations corresponding to the current Eq. (7). Klemens, in his Eq. (6.38), gives the result

$$\tau_u^{-1} = \sum_{\mathbf{q}',\mathbf{q}''} A_{\mathbf{q},\mathbf{q}',\mathbf{q}''} \frac{\mathbf{\lambda} \cdot \mathbf{b}}{\mathbf{\lambda} \cdot \mathbf{q}} (N_0' + N_0'' + 1), \qquad (8)$$

where **b** is an inverse lattice vector, and where Klemens' notation convention requires that $(N_0'+N_0''+1)$ must be replaced by $(N_0'-N_0'')$ for events of class I. Thus the temperature exponents of τ_N^{-1} and τ_u^{-1} are both bounded by the extremes of the temperature exponents of $(N_0'-N_0'')$ and $(N_0'+N_0''+1)$. We shall distinguish between the two bracketed functions by using a notation involving $m_{\rm I}$ and $m_{\rm II}$, where $(N_0'-N_0'') \propto T^{m_{\rm I}}$ and $(N_0'+N_0''+1) \propto T^{m_{\rm II}}$.

We wish to find the extreme values of m_{I} , where m_{I} is defined by

$$N_0' - N_0'' \propto T^{m_{\rm I}}.$$
 (9)

We shall use a notation where $h\nu'K_B^{-1}T^{-1} = x_1$ and $h\nu''K_B^{-1}T^{1} = x_2$, while $h\nu K_B^{-1}T^{-1} = x$.

By applying Corollary II and the definition in Eq. (1) to the expression in Eq. (9), we obtain

 $N_0' \propto T^{\iota'}$,

$$m_{\rm I} = (N_0'l' - N_0''l'') / (N_0' - N_0''), \qquad (10)$$

where l' and l'' are defined by

and

$$N_0'' \propto T^{\iota''}.$$
 (11b)

(11a)

In Eq. (10), m_1 is easily recognized as the slope of a secant line between two points on the curve which is a plot of N_0l versus N_0 . By the mean-value theorem of differential calculus, the extreme values of the slope of the secant line are bounded by the extremes of the slope of the tangent to the curve. The extremes of the slope of the tangent, $d(N_0l)/dN_0$, occur either at the ends of the allowed region or at some place or places where $d^2(N_0l)/dN_0^2$ is equal to zero. The immediate problem then is to express N_0l as a function of N_0 exclusively. By direct application of Eq. (1) we find

$$l = xe^{x}/(e^{x}-1) = xe^{x}N_{0}.$$
 (12)

Substituting $(N_0+1)/N_0$ for e^x and substituting $\ln(1+N_0^{-1})$ for x, we find

$$N_0 l = N_0 (N_0 + 1) \ln(1 + N_0^{-1}).$$
(13)

The first derivative of $N_0 l$ with respect to N_0 is easily found directly and is given by

$$d/dN_0(N_0l) = (2N_0+1)\ln(1+N_0^{-1})-1, \quad (14)$$

while the second derivative is given by

$$\frac{d^2}{dN_0^2}(N_0 l) = 2 \ln\left(\frac{N_0 + 1}{N_0}\right) - \frac{2N_0 + 1}{N_0(N_0 + 1)}.$$
 (15)

From this last equation, it is found that $d^2(N_0l)/dN_0^2$ varies as

$$\left[-(3N_0^3)^{-1}+(2N_0^4)^{-1}\right]$$

at large N_0 , and is therefore negative. For very small N_0 , $d^2(N_0l)/dN_0^2$ varies as $(-N_0^{-1}-2N_0)$, which is also negative. A check of intermediate regions reveals that the second derivative is negative everywhere⁶ for positive N_0 . Consequently, the extremes of the slope of (N_0l) versus N_0 occur at the ends of the allowed interval, and the extreme values of Eq. (10) are given by the extreme values of Eq. (14), evaluated at the extreme values of x.

Combining Equations (10) and (14) by use of the differential calculus mean-value theorem and resubstituting to get the result in terms of x, rather than in terms of N_0 , we obtain

$$m_1 = x[2/(e^x - 1) + 1] - 1,$$
 (16)

where x has some value $x_1 < x < x_2$. The extremes of m_I are given in the limit where $x_1 = x_2 = 0$ or $x_1 = x_2 = x_{max}$ in the case where we are putting limits on m for a relaxation time expression which is to be used for an entire polarization of acoustic phonons, including those with $\nu \approx 0$. When $x_1 = x_2 = 0$, m_I equals unity, and when $x_1 = x_2 = x_{max}$, we find that

$$(m_{\rm I})_{\rm max} = x_{\rm max} [2(e^{x_{\rm max}} - 1)^{-1} + 1] - 1.$$
 (17)

In a III-V compound, to be sure of including the most extreme temperature variation of the scattering, we must evaluate Eq. (17) for x_{max} equal to the x value of optical phonons having k equal to zero.

Some interesting conclusions may be drawn from the fact that the right side of Eq. (15) is always negative for $N_0>0$. It follows that dm_1/dx_1 and dm_1/dx_2 are both positive in the range $0 < x_1 < x_2 < x_{max}$. This follows from Eq. (10) and the fact that $(dN_0)/dx < 0$. A graph of $N_0 l$ versus N_0 appears in Fig. 1. It is obvious from the graph that the extreme slopes of the secant occur when the secant line is shortened to a tangent at the ends of the allowed interval in N_0 .

It is conceivable that the extremes of m could be desired for a relaxation-time expression where the expression is applied to phonons in a limited energy range, not including $\nu = 0$. In this case, we may not set $x_1 = x_2$. However, we still benefit from the fact that

$$(dm_{\mathrm{I}}/dx_{1})_{x_{2} \mathrm{ const}} > 0$$
 and $(dm_{\mathrm{I}}/dx_{2})_{x_{1} \mathrm{ const}} > 0$.

The extreme values of $m_{\rm I}$ then come directly from Eq. (10). We find that x_1 and x_2 must assume minimum simultaneous allowed values in order to obtain $(m_{\rm I})_{\rm min}$ and maximum simultaneous allowed values in order to

⁶ The third derivative of $N_0 l$ with respect to N_0 is found to be $N_0^{-2}(N_0+1)^{-2}$. This quantity is obviously always greater than $N_0 l$ zero in the region $0 < N_0 \le \infty$. Therefore the second derivative of with respect to N_0 is monatonically increasing in the same region, and since it is negative at both end points, it is negative throughout the region.



FIG. 1. $N_0 l$ versus N_0 . This plot has the significance that the slope of a secant line gives the value of m for the corresponding class I annihilation event (annihilation by combination). That is, the process Ph+Ph₁ \rightarrow Ph₂ (Ph=phonon) provides a contribution to τ_{3p}^{-1} where the particular contribution has a temperature exponent, m, given by the slope of the secant line connecting the points $[N_0(x_2), N_0(x_2)l(x_2)]$ and $[N_0(x_1), N_0(x_1)l(x_1)]$ in the graph above.

obtain $(m_{\rm I})_{\rm max}$. For both these extremes, in this case, (x_2-x_1) will be equal to $K_B^{-1}T^{-1}h\nu_{\rm min}$, where $\nu_{\rm min}$ is the lowest energy phonon of the energy region under study

for the polarization of interest. The values of x_1 and x_2 are not restricted to the x values available to the heat carrying phonons in the energy range under study, since the values x_1 and x_2 are the x values for the scattering phonon and resultant phonon.

For the phonon-splitting events (class II), the analytic manipulation has been less satisfying. However, it has been found possible to obtain analytic bounds on m_{II} .

We shall assume $x_2 > x_1$, and note that $x_2+x_1 \le x_{\max \text{ acoustic}}$ for the solid. For notational purposes, we call $(x_1+x_2)/2 = x/2 = x_0$. We define a parameter r such that $x_1 = x_0(1-r)$ and $x_2 = x_0(1+r)$ where 0 < r < 1, and note that $0 < x_0 < 0.5x_{\max \text{ acoustic}}$. We are assuming that we are working with a relaxation-time expression which is applied to an entire acoustic polarization.

Our plan in finding the extremes of $m_{\rm II}$ is to fix x_0 and vary r, (0 < r < 1), to find restricted extremes of $m_{\rm II}$ with fixed x_0 . After obtaining an analytic expression for this restricted extreme of $m_{\rm II}$ with fixed x_0 , we shall vary x_0 , $(0 < x_0 < 0.5x_{\max ac})$, to obtain the ultimate extreme values of $m_{\rm II}$.

We have previously defined m_{II} as

$$(N_0' + N_0'' + 1) \propto T^{m_{11}}, \tag{18}$$

where the meaning of such a statement is given by Eq. (1).

Before attacking the computation of $m_{\rm II}$ in Eq. (18), one should note that Corollary II may be generalized to three or more functions. Applying this to Eq. (18), and remembering $1 \propto T^0$, we find that

$$m_{\rm II} = (N_0'l' + N_0''l'')(N_0' + N_0'' + 1)^{-1}.$$
 (19)

In Eq. (19), l' and l'' are as defined in Eqs. (11a) and (11b) and have the values given in Eq. (12). If we substitute these values for l' and l'', and then substitute $(1+r)x_0$ for x_2 and $(1-r)x_0$ for x_1 , we obtain

$$m_{\rm II} = \frac{x_0 \left[(1-r)e^{x_0(1-r)} \left\{ e^{x_0(1-r)} - 1 \right\}^2 + (1+r)e^{x_0(1-r)} \left\{ e^{x_0(1-r)} - 1 \right\}^2 \right]}{\left\{ e^{x_0(1-r)} - 1 \right\} \left\{ e^{x_0(1+r)} - 1 \right\} \left\{ e^{2x_0} - 1 \right\}}.$$
(20)

It would be convenient to find dm_{II}/dr formally and locate all its zeros in the region 0 < r < 1. Symmetry arguments yield an obvious zero for dm_{II}/dr at r=0, but no proof has been found that this single zero exhausts the supply.

It is possible to compute m_{II} for a net of values of x_0 and r and observe the way in which m_{II} varies with rfor various fixed values of x_0 . This has been done for all combinations of $r=0, 0.1, 0.2, \dots 0.9, 1.0,$ and $x_0=0,$ $0.1, 0.2, \dots 0.9, 1.0, 2.0, 3.0, \dots 10.0$. Selected points in this net are given in Table I. The omitted points reveal no additional features and were excluded for reasons of space. Within the range $0 \le r \le 1, 0 \le x_0 \le 10$, it appears that the extremes of m_{II} are obtained when r=0 and r=1, for any fixed value of x_0 . Applying this to Eq. (20), we find that the limited extremes of m_{II} for fixed x_0 are given by

$$1 > m_{\rm II} > 2x_0 e^{x_0} (e^{2x_0} - 1)^{-1}.$$
(21)

We shall assume that this expression is valid for all values of x_0 , even though it has been checked computationally only for $x_0 < 10$. This matter can only be of concern if a significant amount of heat is carried by phonons having $h\nu > 20$ KT, which is unlikely. As we vary x_0 in the range available to acoustic phonons at the given temperature, we find that the ultimate extremes of $m_{\rm II}$ for the entire acoustic frequency range for ν in the solid are given by

 $1 > m_{II} > x_{\max ac}$

$$\times \exp(0.5x_{\max ac}) [\exp(x_{\max ac}) - 1]^{-1}.$$
 (22)

$x_0 \rightarrow r \downarrow$	0	0.1	0.2	0.6	1.0	5.0	10.0
0 0.1 0.3 0.5 0.7 0.9 1.0	$\begin{array}{c} 1.000 - 0 \\ 1.000 - 0 \\ 1.000 - 0 \\ 1.000 - 0 \\ 1.000 - 0 \\ 1.000 - 0 \\ 1.000 - 0 \end{array}$	$\begin{array}{r} 9.983 - 1 \\ 9.984 - 1 \\ 9.984 - 1 \\ 9.988 - 1 \\ 9.992 - 1 \\ 9.997 - 1 \\ 1.000 - 0 \end{array}$	$\begin{array}{r} 9.934 - 1 \\ 9.934 - 1 \\ 9.940 - 1 \\ 9.950 - 1 \\ 9.966 - 1 \\ 8.987 - 1 \\ 1.000 - 0 \end{array}$	$\begin{array}{r} 9.424 - 1 \\ 9.430 - 1 \\ 9.476 - 1 \\ 9.569 - 1 \\ 9.707 - 1 \\ 9.891 - 1 \\ 1.000 - 0 \end{array}$	$\begin{array}{r} 8.509 - 1 \\ 8.524 - 1 \\ 8.645 - 1 \\ 8.885 - 1 \\ 9.244 - 1 \\ 9.720 - 1 \\ 1.000 - 0 \end{array}$	$\begin{array}{c} 6.738 - 2 \\ 7.267 - 2 \\ 1.183 - 1 \\ 2.273 - 1 \\ 4.321 - 1 \\ 7.710 - 1 \\ 1.000 - 0 \end{array}$	$\begin{array}{r} 9.080 - 4 \\ 1.295 - 3 \\ 6.418 - 3 \\ 3.392 - 2 \\ 1.572 - 1 \\ 5.820 - 1 \\ 1.000 - 0 \end{array}$

TABLE I. Results of computation of m_{II} , using Eq. (20) of the text. The values are tabulated in the manner of a computer output, using power-of-ten notation. Thus 9.988 -1 is to be interpreted as 9.988×10^{-1} . The results give the temperature exponent of the temperature dependence of a phonon-splitting event of the three-phonon type.

When Eq. (22) is applied to the transverse branch, it is necessary to use $x_{\text{max transverse}}$ in place of $x_{\text{max ac}}$.

In the case where Eq. (22) is applied to a limited energy range of a polarization, $x_{\max ac}$ must be replaced by $x_{\max, \text{ energy range}}$. In such an application, the upper limit on m_{II} is still found to be unity.

For any given solid, if the three-phonon relaxation time for either normal or umklapp events is given by $\tau_{3P}^{-1} \propto T^m$, then for an entire acoustic polarization, including $\nu = 0$, *m* is bounded by the maximum value of Eq. (17) and the minimum value of Eq. (22), giving the relation

$$x_{\max \text{ opt}} \{2[\exp(x_{\max \text{ opt}}) - 1]^{-1} + 1\} - 1 > m, \qquad (23)$$
$$m > x_{\max \text{ ac}} \exp(0.5x_{\max \text{ ac}}) [\exp(x_{\max \text{ ac}}) - 1]^{-1}.$$

III. APPLICATION TO GaAs, InSb, Si, AND Ge

The relations just developed may be used to establish temperature dependent upper and lower bounds on m in relations of the type $\tau_{3P}^{-1} \propto T^m$ in Ge, Si, GaAs, and InSb. In doing this, we shall also establish a temperature range for the validity for some relaxation time relations originally derived by Herring.² It should be noted that Herring implied limits which agree reasonably well with those which we shall develop.

Herring derived a relation for the temperature dependence of the relaxation time $\tau_{L,3P}$ for longitudinal phonons relaxing via three-phonon events. He found that $\tau_{L,3P}^{-1} \propto \omega^2 T^3$ in III-V compounds at low temperatures. A similar relation for transverse phonons relaxing via three-phonon processes was found to be $\tau_{\text{tran}, 3P}^{-1} \propto \omega T^4$ (valid for III-V compounds at low temperatures). In the present notation, this means m=3 for longitudinal phonons and m=4 for transverse phonons, for three-phonon processes.

From Eq. (22), we see that three-phonon events of class II cannot contribute to τ_{3P}^{-1} in such a way as to make *m* larger than unity. The relatively high values of *m* mentioned in the Herring expressions must be due to events of class I (annihilation by combination). From Eq. (17) and Theorem I, we see that these values of *m* require the involvement of values of ν'' such that x_2 is greater than 3.85 for m=3, and require values of ν'' such that x_2 is greater than 4.9 in order to obtain m=4.

A careful reading of the Herring derivations reveals a reliance on a lack of dispersion in the development of the basic expression $\tau(\lambda q, \lambda T) \propto \lambda^{-5}$ which is the basis of his expression $\tau^{-1}(q_0) \propto q_0 \alpha T^{5-\alpha}$. This latter relation is the basis of the relations $\tau_{L,3P}^{-1} \propto \omega^2 T^3$ and $\tau_{\text{tran}, 3P} \propto \omega T^4$. This would limit x_2 to values such that ν'' is less than $\nu_{\text{Eax nondispersive}}$. For the relation $\tau_{\text{tran}, 3P}^{-1} \propto \omega T^4$, we now have the dual requirements

$$x_{2 \max} > 4.9$$
, $\nu''_{\max} < \nu_{\max}$ nondispersive.

Similarly, for the relation $\tau_{L,3P}^{-1} \propto \omega^2 T^3$, we have the dual requirements

$$x_{2 \max} > 3.85$$
, $\nu''_{\max} < \nu_{\max}$ nondispersive

For Ge,⁷ however, severe dispersion appears in the

TABLE II. Limits on the validity of various relations of the type $\tau_{3P}^{-1} \propto T^m$. The limitations shown in the first two columns are due to the interaction of heat-carrying phonons with other phonons inhabiting regions of the phonon spectrum exhibiting dispersion. The limitations in the last three columns are due to a complete lack of three-phonon processes having the indicated temperature dependence.

Material	Assumptions of ωT^4 relation invalid for $T>$	Assumptions of $\omega^2 T^3$ relation invalid for $T >$	$\tau_{3P}^{-1} \propto T^m$ where $m < 4$ if $T >$	$ \begin{array}{c} \tau_{sP}^{-1} \propto T^{m} \\ \text{where } m < 3 \\ \text{if } T > \end{array} $	$\tau_{3P}^{-1} \propto T^{m}$ where $m < 2$ if $T >$
InSb	13°K	16.5°K	54°K	69°K	103°K
GaAs	20°K	26°K	85°K	108°K	159°K
Ge	20°K	26°K	90°K	115°K	167°K
Si	43°K	55°K	149°K	190°K	282°K

⁷ B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958).



FIG. 2. Boundaries of the temperature exponent in the temperature dependence of three-phonon relaxation processes in Si. Three-phonon events contributing either to umklapp relaxations or to N-type single-mode relaxations all contribute temperature dependences within the indicated bounds. Splitting events (class II) contribute so as to weight m in the region between the lower bound and the value m=1. Events causing annihilation via combination (class I) contribute in such a manner as to weight min the region between the value m=1 and the value shown by the upper boundary curve.

(1,0,0) direction at frequencies below 2×10^{12} sec⁻¹. From this we may deduce that the Herring derivation of the ωT^4 relation for transverse phonons in Ge is only soundly based when $T < 20^{\circ}$ K. Similarly, for the $\tau_{L,3P}^{-1} \propto \omega^2 T^3$ relation in Ge, we find the requirement, $T < 26^{\circ}$ K.

Since the phonon-dispersion curves of GaAs⁸ resemble those of Ge,⁷ we find that similar calculations for GaAs yield temperatures almost identical to the two just given. The corresponding temperatures in Si and InSb are given in Table II, where the Si values are based on phonon-spectrum information derived from neutron studies,⁹ while the InSb values are based on information derived from optical studies.¹⁰

Although the specific temperatures just mentioned do not appear in the original article by Herring,² the text of the article clearly points out that the expressions are only intended for use at low temperatures. The text contains comments which may be used to derive temperature limits for the application of the $\tau_{L,3P}^{-1} \propto \omega^2 T^3$ law in Ge, when one combines Herring's comments with the currently known features of the Ge-phonon spectra.⁷ The limits thus derived are approximately the same as those given above. Unfortunately, the lack of any other reliable expression for the temperature dependence of $\tau_{L,3P}^{-1}$ and $\tau_{\text{tran, }3P}^{-1}$ has led to a widespread use of the Herring relations at inappropriate temperatures.

A few limiting relations derived from Eq. (17) have been tabulated for Ge, Si, GaAs, and InSb in Table II, in addition to the limits for the validity of the Herring relation.



FIG. 3. Boundaries of the temperature exponent in the temperature dependence of three-phonon relaxation processes in GaAs. Three-phonon events contributing either to umklapp relaxations or to N-type single-mode relaxations all contribute temperature dependences within the indicated bounds. Splitting events (class II) contribute so as to weight m in the region between the lower bound and the value m=1. Events causing annihilation via combination (class I) contribute in such a manner as to weight m in the region between the value m=1 and the value shown by the upper boundary curve.

For Si and GaAs, both upper and lower limits for m have been calculated from Eqs. (17) and (22) for $\tau_{L,3P}^{-1}$ and $\tau_{\text{tran, }3P}^{-1}$, using information on the phonon spectra now available in the literature.^{8,9} These limits on m for Si and GaAs are presented graphically in Figs. 2 and 3.

One might conceive of the possibility of using something similar to a Callaway³ approach to thermalconductivity calculations in an effort to assign specific fractions of the heat conduction to specific polarizations of phonons at the various temperatures.^{11,12} This would involve curve-fitting of thermal-conductivity data, using reasonable but distinguishably different assumed functional forms for the relaxation-time functional expressions for the separate polarizations. The fractional assignment actually arrived at would depend upon the temperature dependence chosen for the relaxation times of the various modes, and would depend upon the extent to which the chosen temperature dependences allowed the calculated thermal conductivity for the specific polarization to conform to the total conductivity observed in the laboratory when the adjustable parameters minimized the discrepancy between the observation and the chosen analytical expression. From Figs. 2 and 3, and Table I, we may appreciate some of the difficulties inherent in such an attempt.

If proper temperature dependences are chosen for the three-phonon relaxation times at high temperatures, it will be difficult to distinguish computationally between the two polarizations, since their values of m must be nearly identical.

⁸ J. L. T. Waugh and G. Dolling, Phys. Rev. 132, 2410 (1963).

⁹ B. N. Brockhouse, Phys. Rev. Letters 2, 256 (1959).

¹⁰ S. S. Mitra, Phys. Rev. 132, 986 (1963).

¹¹ M. G. Holland, Phys. Rev. 132, 2461 (1963).

¹² C. M. Bhandari and G. S. Verma, Phys. Rev. 140, A2101 (1965).

At very low temperature, the Herring relations² may be used, and the two polarizations are noticeably distinct regarding their three-phonon relaxation times. However, at these temperatures the boundary and isotope scattering are important, and the three-phonon scattering does not strongly enter into the temperature dependence of the total relaxation time for most phonons of either polarization. Therefore, even at these temperatures, the total conductivity will be composed of two contributions (one from each polarization) which differ only slightly in functional form. This difference may be so slight as to be of limited use from a computational standpoint; i.e., it might require data of an accuracy which is unobtainable.

If quite noticeably different relaxation-time functional dependences are used for $\tau_{L,3P}^{-1}$ and $\tau_{\text{tran, }3P}^{-1}$ over most of the temperature range of the available data, calculations of the type alluded to may be performed, and quite noticeably differing conductivity contributions will be assigned to the separate polarization, but the results will be in error. To understand these errors, we must understand the Callaway³ method of calculating thermal conductivity.

In using Callaway's method, when one desires the contribution of a phonon state to the total thermal conductivity, the heat capacity of the phonon state, the square of the group velocity, and a constant factor are to be multiplied by a relaxation time designated as α . The relation of α to the other relaxation times is given by

$$\alpha = \tau_c [1 + (\beta/\tau_N)], \qquad (24)$$

where τ_c is given by

$$\tau_{c}^{-1} = \tau_{i}^{-1} + \tau_{B}^{-1} + \tau_{u}^{-1} + \tau_{N}^{-1}.$$
 (25)

In the equations above, τ_i is the isotope scattering relaxation time, τ_B is the boundary scattering relaxation time, τ_N is that due to normal scattering, τ_u is the three-phonon umklapp scattering relaxation time, and β is a particular type of average value of the relaxation time associated with all scattering processes which are not momentum-conserving.

In most recent calculations^{11,12} using the Callaway method, it has been assumed that β is zero in equations similar to Eq. (24). Such an assumption is a practical necessity from a computational standpoint, and we shall continue the analysis on this basis. It is obvious that this assumption implies that α is identical to τ_c at all temperatures. This equivalence implies that at high temperatures where τ_i^{-1} and τ_B^{-1} are negligible, the temperature dependence of α^{-1} and τ_c^{-1} is that of $(\tau_u^{-1} + \tau_N^{-1})$.

 $(\tau_u^{-1} + \tau_N^{-1})$. This last point would be true at high temperatures even if β were not assumed to be zero. At high temperatures, the principal contribution to β^{-1} is from phononphonon umklapp processes. Therefore, the temperature dependence of β is the same as that of τ_u . Since both τ_u and τ_N vary as T^{-1} at high temperatures, the quantity $(1+\beta/\tau_N)$ becomes temperature independent, and $\alpha^{-1} \propto \tau_c^{-1}$. The errors incurred by assuming this to be true might be expected to be much less serious than those created by setting β equal to zero.

A Callaway-type analysis is usually restricted to boundary and defect scattering and to three-phonon events arising from anharmonicities. For reasonably large crystals of pure unstrained materials, the relaxation time is then largely determined by the threephonon processes at temperatures noticeably greater than those associated with the maximum in κ . Simultaneous and nearly identical errors in the temperature exponent of τ_N and τ_u consequently appear directly as similar errors in the temperature exponents of α and κ at the higher temperatures.

The exponent in the relation¹³ $\tau^{-1} \propto T^m$ at the higher temperatures appears in an obvious way in a plot of log κ versus log T, since the heat capacity of each phonon state is then temperature independent, and the temperature dependence of κ is derived solely from the temperature dependence of τ , which is the negative of the temperature dependence of τ^{-1} . That is, if $\kappa \propto T^P$, then $\tau \propto T^P$ and $\tau^{-1} \propto T^{-P}$. At high temperatures, such a value of P is consequently given by the slope of the log κ -versus-log T curve.

The most obvious consequence of the use of the Herring relations at high temperatures is that the incorrect temperature dependence of τ_{3P} causes κ to decrease rapidly with temperature, for the polarization receiving the incorrect treatment. This leads to the erroneous impression that such a polarization has a conductivity whose relative importance declines rapidly with increasing temperature, at the higher temperatures.

At high temperatures, the nearly identical values for m for the longitudinal and transverse polarizations, as indicated in the present work, would require nearly identical slopes of $\kappa(\text{transv})$ and $\kappa(\log)$ at high temperatures, on a plot of $\log \kappa$ versus $\log T$. This means that $\lfloor \log \kappa(\text{tran}) - \log \kappa(\log) \rfloor$ is independent of temperature, and the ratio of these partial conductivities is independent of temperature.

In spite of the difficulties discussed, it is conceivable that a very careful derivation of the actual three-phonon relaxation time expressions could be used in conjunction with phonon-dispersion curve information to obtain a fractional assignment of heat conduction to separate phonon polarizations, using a Callaway approach. However, if we presume the availability of experimental data which is reliable and accurate to the required number of significant digits, we must remember that an additional difficulty exists, viz., the numerical results of the analysis might be quite sensitive to the particular assumption of the importance of four-phonon events.

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¹³ Where, by τ^{-1} , we mean α^{-1} , τ_c^{-1} , or $(\tau_{N,3R}^{-1} + \tau_{u,3P}^{-1})$ since all three statements are nearly equivalent at high temperatures, if we ignore four-phonon processes.