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Three-Phonon Scattering and Guthrie's Limits for Its Temperature Dependence*

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It is shown that one can explain the temperature dependence of the phonon conductivity of Ge in the entire range from 2 to 1000 °K if the three-phonon relaxation rate is given by $\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} e^{-\Theta/\alpha T}$. Three-phonon scattering processes are classified, after Guthrie, into two groups: class I, which involves the annihilation of carrier phonons by combination, and class II, which involves splitting of carrier phonons. At all temperatures, the values of $m(T)$ for both classes of processes lie either definitely below or close to the upper limit of $m(T)$ as obtained by Guthrie.

I. INTRODUCTION

Recently Guthrie[1] has given an expression for the three-phonon relaxation rate in the form

$$\tau_{3ph}^{-1} \propto g(\omega) f(T) \quad , \tag{1}$$

where $f(T) = T^m$ and $m = m(T)$. Further, $g(\omega) = \omega$ for transverse phonons, and $g(\omega) = \omega^2$ for longitudinal phonons. The value of m is found to be the same for both normal and umklapp processes. However, Klemens[2-4] has given an expression for umklapp processes:

$$\tau_{3ph}^{-1} \propto g(\omega) T^m e^{-\Theta/\alpha T} \quad . \tag{2}$$

At low temperatures he has taken $m = 4$ for transverse phonons and $m = 3$ for longitudinal phonons. These temperature dependences are in agreement with the findings of Herring.[5] At high temperatures, Klemens took $m = 1$ for both polarization branches. Except Joshi and Verma,[6] who have taken different values of m in the different temperature ranges ($m = 1-4$ for transverse phonons and $m = 1-3$ for longitudinal phonons), other workers have used the expressions given by Herring and Klemens. Since m, according to Guthrie, is a continuous function of temperature, $m = m(T)$, the use of different values of m in the different temperature regions is only a partial solution of the problem. In view of this inadequacy, we prefer to incorporate Guthrie's idea of the temperature dependence of m by writing the three-phonon scattering relaxation rate as

$$\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} e^{-\Theta/\alpha T} = B g(\omega) T^{m(T)} e^{-\Theta/\alpha T} \quad . \tag{3}$$

This expression differs from Klemens's in that here m is a function of temperature, and one does not assign discrete values to m (e.g., $m=4$ or 3 at low temperatures and $m=1$ at high temperatures).

According to Guthrie, thermal transport by phonons takes place in two different ways: class I events in which the heat carrier phonon is annihilated by combination of phonons and class II events in which the carrier phonon is annihilated by splitting. This classification leads to participation of transverse phonons alone in class I events whereas longitudinal phonons participate in both the events, class I as well as class II. However, Guthrie has not given any procedure to find out $m(T)$ except that he has given the upper and lower bounds of m. The only other hints are that m, besides its dependence on the temperature, varies with the nature of the events as well as the polarization. In view of the fact that m can lie anywhere between its upper and lower bounds, there still remains a great amount of uncertainty in taking any suitable value of m. To avoid these uncertainties, we define $m_{\mathrm{av}}(T)$, which is given by

$$[m_{\mathrm{av}}(T)]_{\mathrm{Guthrie}} = \tfrac{1}{2}[m_{\text{upper bound}}(T) + m_{\text{lower bound}}(T)] \ . \tag{4}$$

The factor $m_{\mathrm{av}}(T)$ is not necessarily equal to the true or correct value of $m(T)$, which is needed to explain the phonon-conductivity results. At high temperatures where both the upper and lower bounds of $m(T)$ approach the same values, the true value of $m(T)$ should be same as the average value of $m(T)$. For low temperatures, where phonon-phonon scattering processes make an appreciable contribution to the thermal resistance, the relation between the true and average values of $m(T)$ can be expressed as

$$T^{[m(T)]^{\mathrm{I,II}}_{\mathrm{True}}} = T^{[m_{\mathrm{av}}(T)]^{\mathrm{I,II}}_{\mathrm{Guthrie}}}(1+\Theta/\alpha T). \tag{5}$$

Obviously for $T \gg \Theta$,

$$[m(T)]^{\mathrm{I,II}}_{\mathrm{True}} = [m_{\mathrm{av}}(T)]^{\mathrm{I,II}}_{\mathrm{Guthrie}} \ .$$

Thus the three-phonon relaxation rate is given by

$$\tau_{3\mathrm{ph}}^{-1} = Bg(\omega)T^{[m(T)]^{\mathrm{I,II}}_{\mathrm{True}}} e^{-\Theta/\alpha T}$$

$$= Bg(\omega)T^{[m_{\mathrm{av}}(T)]^{\mathrm{I,II}}_{\mathrm{Guthrie}}}(1+\Theta/\alpha T)e^{-\Theta/\alpha T} \ . \tag{6}$$

At high temperatures, $e^{-\Theta/\alpha T} \to 1$, $\Theta/\alpha T \ll 1$, and $[m_{\mathrm{av}}(T)]^{\mathrm{I,II}}_{\mathrm{Guthrie}} \to 1$. Hence Eq. (6) gives

$$\tau_{3\mathrm{ph}}^{-1} = Bg(\omega)T \quad \text{for } T \gg \Theta \ , \tag{7}$$

which is the well-known result of Klemens, Holland, [7] and Guthrie in semiconductors in the high-temperature region. At low temperatures, $\Theta/\alpha T \gg 1$ and $\tau_{3\mathrm{ph}}^{-1}$ is given by

$$\tau_{3\mathrm{ph}}^{-1} = B'g(\omega)T^{(m_{\mathrm{av}}-1)}e^{-\Theta/\alpha T} \ , \tag{8}$$

where $B' = B\Theta/\alpha$. If $g(\omega)=\omega^2$ and $m_{\mathrm{av}}=4$, then it reduces to the well-known result of Klemens and Herring,

$$\tau_{3\mathrm{ph}}^{-1} = B'\omega^2 T^3 e^{-\Theta/\alpha T}$$

for longitudinal phonons at low temperatures.

The choice of the relations, Eqs. (5) and (6), is guided by the high- and low-temperature approximations of the temperature dependence of three-phonon relaxation rate as obtained by Peierls, [8] Herring, [5] Klemens, [2-4] Holland, [7] and Guthrie. [1] These two approximations are contained in the factor $(1+\Theta/\alpha T)$ in terms of $T \gg \Theta$ and $T \ll \Theta$. For intermediate temperatures or for $T \sim \Theta$, both the terms of the factor $(1+\Theta/\alpha T)$ are important. The greatest support for the single relation for the temperature dependence of the three-phonon relaxation rate in the entire temperature range 2–1000 °K comes from the fact that it explains the phonon-conductivity results for Ge very well over the whole range. Use of Eqs. (5) and (6) is necessary as long as one wants to incorporate the average values of m obtained by Guthrie for the correct description of the temperature dependence of three-phonon relaxation rate.

Holland[7] was the first to distinguish between longitudinal and transverse phonons as separate carriers of thermal energy. He also took into account the dispersion of different phonon branches. However, he used $q=\omega/v$ in replacing v_g/v_p^2 by $1/v$ in the conductivity integrals for longitudinal phonons and for transverse phonons. For this we have used a much more realistic relation given by[9]

$$\vec{q} = (\omega/\vec{v})(1+\gamma\omega^2) \ , \tag{9}$$

where γ is a constant, which can be calculated from the dispersion curve by the relation

$$\gamma = (1/\omega^2)(qv/\omega - 1) \ . \tag{10}$$

Then v_g/v_p^2 is replaced by

$$\frac{1}{v}\,\frac{(1+\gamma\omega^2)^2}{(1+3\gamma\omega^2)}$$

in the conductivity integrals. If there is no dispersion in the phonon branch, $\gamma=0$, then $v_g/v_p^2 = 1/v$ as taken by Holland.

There is another very important aspect of the present calculations. This will be more evident if we reproduce Guthrie's table for Si and Ge (see Table I).

This shows that the temperature dependence of the three-phonon relaxation rate has not been taken into account properly in the earlier calculations of phonon conductivity of Ge or Si. However, in the present calculations m is a continuous function of temperature and is either below or close to the

TABLE I. Guthrie's limits for the exponent m for Ge and Si.[a]

Material	Assumption of ωT^4 relation invalid for $T>$ (°K)	Assumption of $\omega^2 T^3$ relation invalid for $T>$ (°K)	$\tau_{3ph}^{-1} \propto T^m$ where $m<4$ if $T>$ (°K)	$\tau_{3ph}^{-1} \propto T^m$ where $m<3$ if $T>$ (°K)	$\tau_{3ph}^{-1} \propto T^m$ where $m<2$ if $T>$ (°K)
Ge	20	26	90	115	167
Si	43	55	149	190	282

[a]See Table II of Ref. 1.

upper limit at different temperatures. Thus the present calculations are the only calculations in which the temperature dependence of the three-phonon relaxation rate has been taken into account properly. In view of the continuous nature of the function $m=m(T)$, the interpretation of the high-temperature data is consistent with low-temperature results, and there is no need to involve different temperature dependences in the different regions. Another significant feature of the present approach is the use of Guthrie's classification of three-phonon scattering events for the first time into the calculations of phonon conductivity.

II. THEORY

Guthrie has classified three-phonon scattering events into two classes, class I in which the carrier phonon is annihilated by combination with other phonons and class II when the carrier phonon is annihilated by splitting. According to Guthrie the three-phonon relaxation rate is given by

$$\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} \quad . \tag{11}$$

The function $g(\omega)$ may be equal to ω^2 for longitudinal phonons and ω for transverse phonons. The most important aspect of this equation is that m is a continuous function of the temperature. Guthrie has obtained the maximum and minimum values of m as a function of temperature for both classes.

For class-I events, we find

$$m_{max}(T) = \{x_{max}[2(e^{x_{max}}-1)^{-1}+1]-1\} \quad , \tag{12}$$

$$m_{min}(T) = 1.0 \quad , \tag{13}$$

where

$$x_{max} = \hbar\omega_{max}/k_0 T \quad .$$

The average value of m for class I events is given by

$$[m_{av}(T)]^{I} = x_{max}(e^{x_{max}}-1)^{-1} + 0.5\, x_{max} \quad . \tag{14}$$

Similarly for class II events, the upper and lower bounds of m are given by

$$m_{max}(T) = 1.0 \quad , \tag{15}$$

$$m_{min}(T) = x_{max}(e^{x_{max}}-1)^{-1} e^{0.5 x_{max}} \quad . \tag{16}$$

Hence the average of m for class II events is given by

$$[m_{av}(T)]^{II} = 0.5\, x_{max} e^{0.5 x_{max}}(e^{x_{max}}-1)^{-1} + 0.5 \quad . \tag{17}$$

In view of the fact that it is not possible to explain the phonon-conductivity results of Ge in the entire temperature range 2–1000 °K, without an exponential factor $e^{-\Theta/\alpha T}$, we have taken Klemens's form for the three-phonon relaxation rate. The three-phonon relaxation rate, which has been successfully used in the present calculation, is of the form

$$\tau_{3ph}^{-1} \propto g(\omega) T^{m(T)} e^{-\Theta/\alpha T}$$

$$= B g(\omega) T^{m(T)} e^{-\Theta/\alpha T} \quad . \tag{18}$$

This expression differs from the expression used by Klemens in the sense that m instead of taking discrete values, say, 4, 3, or 1, is a continuous function of the temperature. This idea is borrowed from Guthrie's work. Further, this differs from Guthrie's expression for τ_{3ph}^{-1} equation (11), which does not contain the exponential factor $e^{-\Theta/\alpha T}$. In three-phonon scattering, the relaxation rate is further expressed as

$$\tau_{3ph}^{-1} = \tau_{3ph}^{-1}(\text{class I}) + \tau_{3ph}^{-1}(\text{class II}). \tag{19}$$

Since class II events are absent for transverse phonons, we have

$$[\tau_{3ph}^{-1}]_{Trans} = B_{T,I}\, T^{m_{T,I}(T)} e^{-\Theta/\alpha T} \quad , \tag{20}$$

where $g(\omega)=\omega$ for transverse phonons. The suffix T for B and m refers to transverse phonons, and suffix I refers to class I events. Similarly, for longitudinal phonons

$$[\tau_{3ph}^{-1}]_{Long} = B_{L,I}\, \omega^2\, T^{m_{L,I}(T)} e^{-\Theta/\alpha T}$$

$$+ B_{L,II}\, \omega^2\, T^{m_{L,II}(T)} e^{-\Theta/\alpha T} \quad , \tag{21}$$

where $g(\omega)=\omega^2$ for longitudinal phonons. The suffix L on B as well as m refers to class II events. For longitudinal phonons both events, class I and class II, are possible.

Taking the ln of both sides of Eq. (5), one ob-

tains the following expressions of $m_{I,II}$ for the different polarization branches:

$$[m(T)]^{T,I}_{True} = m_{T,I}(T) = [m_{av}(T)]^{T,I}_{Guthrie} + \frac{\ln(1+\Theta/\alpha T)}{\ln T},$$

$$[m(T)]^{L,I}_{True} = m_{L,I}(T) = [m_{av}(T)]^{L,I}_{Guthrie} + \frac{\ln(1+\Theta/\alpha T)}{\ln T}, \quad (22)$$

$$[m(T)]^{L,II}_{True} = m_{L,II}(T) = [m_{av}(T)]^{L,II}_{Guthrie} + \frac{\ln(1+\Theta/\alpha T)}{\ln T},$$

where Θ is the Debye temperature. Further the values of $m_{av}(T)$ for the different polarization branches can be obtained from Eqs. (14) and (17). Thus

$$[m_{av}(T)]^{T,I}_{Guthrie} = x_{max,T}(e^{x_{max,T}} - 1)^{-1} + 0.5\, x_{max,T},$$

$$[m_{av}(T)]^{L,I}_{Guthrie} = x_{max,L}(e^{x_{max,L}} - 1)^{-1} + 0.5\, x_{max,L}, \quad (23)$$

$$[m_{av}(T)]^{T,II}_{Guthrie} = 0.5\, x_{max,T}\, e^{0.5 x_{max,T}} \times (e^{x_{max,T}} - 1)^{-1} + 0.5,$$

where

$$x_{max,L} = \hbar\omega_{max,L}/k_0 T, \quad x_{max,T} = \hbar\omega_{max,T}/k_0 T,$$

and $\omega_{max,L}$ and $\omega_{max,T}$ are the zone-boundary frequencies for the longitudinal- and transverse-phonon branches. Since the values of $[m_{av}(T)]^{T,I}_{Guthrie}$, $[m_{av}(T)]^{L,I}_{Guthrie}$, and $[m_{av}(T)]^{T,II}_{Guthrie}$ can be calculated with the help of Eqs. (23), values of $m_{T,I}(T)$, $m_{L,I}(T)$, and $m_{L,II}(T)$ are known from Eq. (22).

Thus in the expression for τ_{3ph}^{-1} for transverse phonons, Eq. (20), there remains only one parameter $B_{T,I}$ and in the similar expression for longitudinal phonons, Eq. (21), there remain two parameters $B_{L,I}$ and $B_{L,II}$, which one has to treat as adjustable parameters.

Assuming the additivity of reciprocal times, the combined relaxation time τ_c is given by

$$\tau_c^{-1} = \sum_i \tau_i^{-1} = \tau_B^{-1} + \tau_{ph}^{-1} + \tau_{3ph}^{-1}, \quad (24)$$

where i refers to ith phonon scattering mechanism. τ_B^{-1} is the inverse of the boundary scattering relaxation time and is given by $\tau_B^{-1} = \bar{v}/LF$, where $\bar{v}$ is the average phonon velocity, L is the characteristic length (given by $L = 1.12S^{1/2}$ for a rectangular cross section S), and F is geometrical factor. The average phonon velocity $\bar{v}$ is given by $\bar{v}^{-1} = \frac{1}{3} \times (2v_T^{-1} + v_L^{-1})$. τ_{ph}^{-1} is the inverse of the relaxation time due to Rayleigh scattering of phonons by the random distribution of point defects such as isotopes. For the mass-difference scattering of phonons this is given by

$$\tau_{ph}^{-1} = A\omega^4 = \left[\frac{V_0}{4\pi\bar{v}^3} \sum_i f_i(1 - m_i/\bar{m})^2\right] \omega^4, \quad (25)$$

where V_0 is the atomic volume, m_i is the mass of the ith species of the atom, f_i is the fractional concentration of the ith species of the atom and $\bar{m}$ is the average atomic mass.

Since we are using average phonon velocities in the calculation of τ_B^{-1} and τ_{pt}^{-1}, they are same for longitudinal phonons and transverse phonons. The combined relaxation time for the transverse phonons is then given by

$$[\tau_c^{-1}]_T = \tau_B^{-1} + A\omega^4 + B_{T,I}\,\omega\, T^{m_{T,I}(T)} e^{-\Theta/\alpha T}. \quad (26)$$

Similarly for longitudinal phonons

$$[\tau_c^{-1}]_L = \tau_B^{-1} + A\omega^4 + B_{L,I}\,\omega^2\, T^{m_{L,I}(T)} e^{-\Theta/\alpha T} + B_{L,II}\,\omega^2\, T^{m_{L,II}(T)} e^{-\Theta/\alpha T}. \quad (27)$$

Since τ_B^{-1} depends upon the geometry and A on the impurity content of the sample, values of τ_B^{-1} and A are fixed for a given sample. Especially in Ge, these two parameters need no adjustment. The experimental results of Ge as obtained by Holland seem to be the good case for the verification of our present ideas of three-phonon relaxation rate and its temperature dependence. Thus values of τ_B^{-1} and A are taken from Holland's paper. There remain, therefore, only three parameters $B_{T,I}$, $B_{L,I}$, and $B_{L,II}$, which may be determined for the best fit between theoretical and experimental values of phonon conductivity in the entire temperature range 2–1000 °K.

Thus, introducing

$$[\tau_{3ph}^{-1}]_{Trans} = B_{T,I}\,\omega T^{m_{T,I}(T)} e^{-\Theta/\alpha T},$$

$$[\tau_{3ph}^{-1}]_{Long} = B_{L,I}\,\omega^2 T^{m_{L,I}(T)} e^{-\Theta/\alpha T} + B_{L,II}\,\omega^2 T^{m_{L,II}(T)} e^{-\Theta/\alpha T}, \quad (28)$$

and

$$\frac{v_g}{v_p^2} = \frac{1}{v}\frac{(1+r\omega^2)^2}{(1+3r\omega^2)}$$

instead of $v_g/v_p^2 = 1/v$, Holland's formulation of two-mode conduction has been modified. We have already mentioned in the introduction that Holland used the relation $\vec{v} = \omega/\vec{q}$ for replacing v_g/v_p^2 by $1/v$, where v_g is the group velocity and v_p is the phase velocity of phonons.

In view of the fact that this is a crude approximation for the dispersion curves for different polarization branches, we have used the relation $\vec{q} = (\omega/\vec{v}) \times (1 + r\omega^2)$ to determine the ratio v_g/v_p^2. This ratio is given by

$$\frac{v_g}{v_p^2} = \frac{(1+r\omega^2)^2}{(1+3r\omega^2)}\frac{1}{v},$$

where r is a constant and can be determined from the dispersion curves. If there is no dispersion in the phonon branch, i.e., $r=0$, $v_g/v_p^2=1/v$, as has been taken by Holland. The expression for the r is

$$r=(1/\omega^2)(qv/\omega-1)\ .$$

The value of r is determined for the regions 0 to $\frac{1}{2}q_{max}$ and $\frac{1}{2}q_{max}$ to q_{max} along two directions, say, [100] and [111], and then its average is taken separately for the two regions. Thus in the case of Ge, we obtain the following values of r[10]: For transverse phonons,

$$[r]_{0\text{ to }q_{max}/2}=2.95\times10^{-27}\ \text{sec}^2\ ,$$

$$[r']_{q_{max}/2\text{ to }q_{max}}=8.28\times10^{-27}\ \text{sec}^2\ ,$$

and for longitudinal phonons,

$$[r'']_{q_{max}/2\text{ to }q_{max}}=1.13\times10^{-27}\ \text{sec}^2\ .$$

TABLE II. Values of the various parameters used in the analysis of phonon conductivity of Ge in the temperature range 2–1000 °K.

$\Theta_1=96$ °K, $\Theta_2=108$ °K, $\Theta_4=208$ °K, $\Theta_3=319$ °K,
$\tau_B^{-1}=1.96\times10^6\ \text{sec}^{-1}$, $B_{T,I}=1.06\times10^{-6}\ \text{deg}^{-m}$
$B_{L,I}=1.78\times10^{-22}\ \text{sec deg}^{-m}$, $B_{L,II}=1.0\times10^{-18}\ \text{sec deg}^{-m}$
$\Theta=376$ °K, $A=2.4\times10^{-44}\ \text{sec}^3$, $F=1.08$

$(V_{T1})_{0<\omega<\omega_1}=3.55\times10^5$ cm/sec
$(V_{T2})_{\omega_1<\omega<\omega_2}=1.30\times10^5$ cm/sec
$(V_{L1})_{0<\omega<\omega_4}=4.92\times10^5$ cm/sec
$(V_{L2})_{\omega_4<\omega<\omega_3}=2.46\times10^5$ cm/sec

As there is no dispersion for longitudinal phonons in the range $0-\frac{1}{2}q_{max}$, i.e., the ω-vs-q curve is a straight line, r is zero for this range. Thus, the modified version of Holland's formulation of phonon conductivity can be expressed as

$$\kappa_T=\frac{2}{3}\frac{k_0}{2\pi^2}\left(\frac{k_0T}{\hbar}\right)^3\left[(v_{T1})^{-1}_{0<\omega<\omega_1}\int_0^{\Theta_1/T}\frac{x^4e^x(e^x-1)^{-2}}{\tau_B^{-1}+\tau_{pt}^{-1}+B_{T,I}\omega T^{m_{T,I}(T)}e^{-\Theta/\alpha T}}\frac{(1+r\omega^2)^2}{(1+3r\omega^2)}\,dx\right.$$

$$\left.+(v_{T2})^{-1}_{\omega_1<\omega<\omega_2}\int_{\Theta_1/T}^{\Theta_2/T}\frac{x^4e^x(e^x-1)^{-2}}{\tau_B^{-1}+\tau_{pt}^{-1}+B_{T,I}\omega T^{m_{T,I}(T)}e^{-\Theta/\alpha T}}\frac{(1+r'\omega^2)^2}{(1+3r'\omega^2)}\,dx\right],\qquad(29)$$

$$\kappa_L=\frac{1}{3}\frac{k_0}{2\pi^2}\left(\frac{k_0T}{\hbar}\right)^3(v_{L1})^{-1}_{0<\omega<\omega_4}\int_0^{\Theta_4/T}\frac{x^4e^x(e^x-1)^{-2}\,dx}{\tau_B^{-1}+\tau_{pt}^{-1}+B_{L,I}\omega^2T^{m_{L,I}(T)}e^{-\Theta/\alpha T}+B_{L,II}\omega^2T^{m_{L,II}(T)}e^{-\Theta/\alpha T}}$$

$$+(v_{L2})^{-1}_{\omega_4<\omega<\omega_3}\int_{\Theta_4/T}^{\Theta_3/T}\frac{x^4e^x(e^x-1)^{-2}}{\tau_B^{-1}+\tau_{pt}^{-1}+(B_{L,I}\omega^2T^{m_{L,I}(T)}+B_{L,II}\omega^2T^{m_{L,II}(T)})e^{-\Theta/\alpha T}}\frac{(1+r''\omega^2)^2}{(1+3r''\omega^2)}\,dx\ .\qquad(30)$$

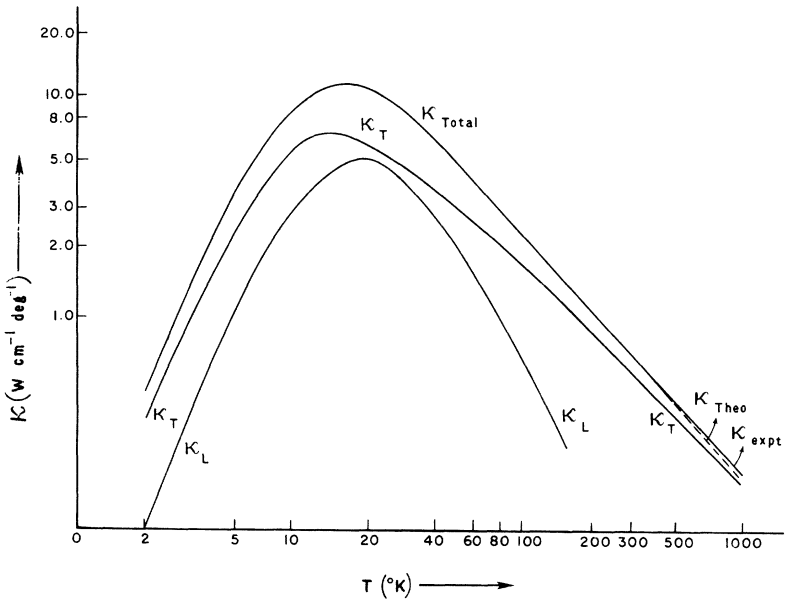

FIG. 1. Comparison of theoretical values of phonon conductivity of Ge with the experimental values in the range 2–1000 °K.

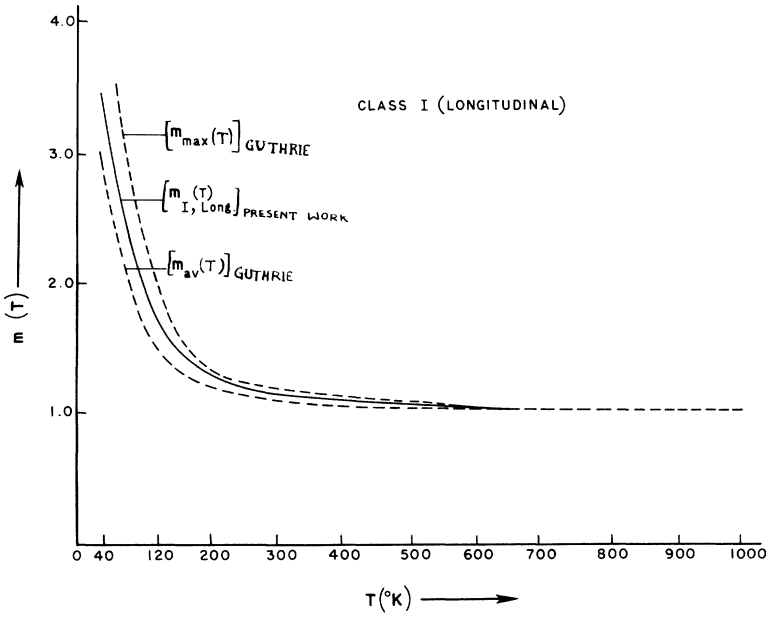

FIG. 2. Temperature dependence of the exponent m for longitudinal phonons for three-phonon class I events. $m_{max}(T)$ is the maximum limit obtained by Guthrie, $m_{av}(T)$ is the average value of $m(T)$ at different temperatures obtained from the maximum and minimum limits of Guthrie, and $m_{L,I}(T)$ is the value used in the present calculations.

The sum of the two contributions κ_L and κ_T represents the observed phonon conductivity κ. In Holland's formulation one of the considerations for having two conductivity integrals for transverse phonons was the fact that umklapp processes start at $\frac{1}{2}q_{max}$. In the present approach the two integrals, both for the transverse as well as longitudinal phonons, are based on the nature of the dispersion curve characterized by the different values of γ and v_{LT}, in the different regions of the ω-vs-q curves.

Assuming that heat transport at high temperatures, say at 1000 °K, is entirely due to transverse phonons, i.e., $\kappa = \kappa_T$, one can adjust the value of the parameter $B_{T,I}$. Using this value of $B_{T,I}$ one can calculate the phonon conductivity κ_T in the entire temperature range. The balance $\kappa - \kappa_T = \kappa_L$ is the contributions due to longitudinal phonons. At temperatures below 100 °K, $m_{L,I} > m_{L,II}$, $T^{m_{L,I}} \gg T^{m_{L,II}}$, and the term containing $T^{m_{L,II}}$ in $(\tau_{3ph}^{-1})_L$ may be neglected. Thus the parameter $B_{L,I}$ is adjusted for κ_L, at 30 °K. Using this value of $B_{L,I}$, one can adjust $B_{L,II}$ such that one can explain κ_L in the entire temperature range. Finally, the sum of κ_L and κ_T is compared with the experimental values of phonon conductivity of Ge as obtained by Holland. If the agreement between theory and experiment is not good in certain regions, the values of the parameters $B_{T,I}$, $B_{L,I}$, and $B_{L,II}$ are again varied slightly in the neighborhood of their previous values for the best possible fit.

III. RESULTS

The values of the various parameters which have been used to calculate the phonon conductivity of Ge in the temperature range 2–1000 °K are given in Table II. The theoretical values of phonon conductivity of Ge are then compared with the experimental values in Fig. 1, which shows the plot of

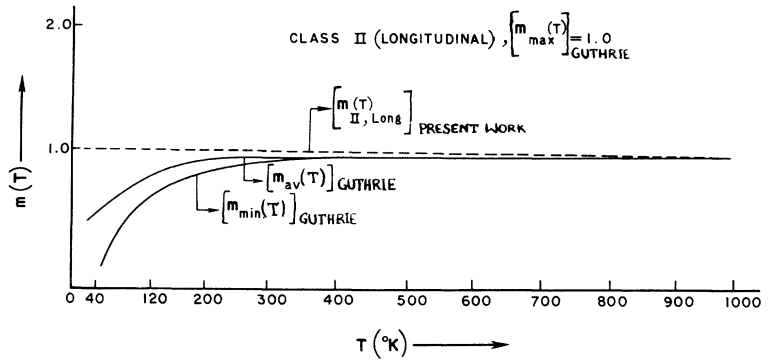

FIG. 3. Temperature dependence of the exponent m for longitudinal phonons for three-phonon class II events. $m_{max}(T)$ is the maximum limit obtained by Guthrie, $m_{av}(T)$ is the average value of $m(T)$ at different temperatures obtained from the maximum and minimum limits of Guthrie, and $m_{L,II}(T)$ is the value used in the present calculations.

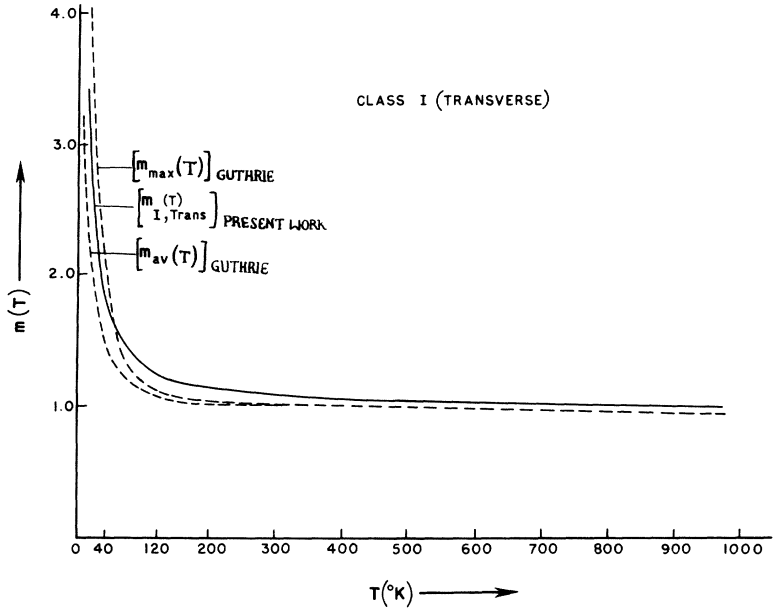

FIG. 4. Temperature dependence of the exponent m for transverse phonons for three-phonon class-I events. $m_{max}(T)$ is the maximum limit obtained by Guthrie, $m_{av}(T)$ is the average value of $m(T)$ obtained from the maximum and minimum limits of Guthrie, and $m_{T,I}(T)$ is the value used in the present calculations.

κ vs T. It may be seen from Fig. 1 that except for the slight deviations in the high-temperature region the agreement is quite good. It may be further noticed from this figure that the major contribution to thermal conductivity comes from transverse phonons. The values of $m(T)$ at different temperatures for transverse and longitudinal phonons as well as for class I and II events are shown in Figs. 2–4. These values of m in general lie either in between the upper and lower bounds or in the neighborhood of the upper bound of m, as obtained on the basis of Guthrie's relations.

It has been shown in the present work that the most appropriate temperature dependence of three-phonon relaxation rate is given by $\tau_{3ph}^{-1} \propto g(\omega) \times T^{m(T)} e^{-\Theta/\alpha T}$. Since m is a continuous function of the temperature, it leads to T^{-1} dependence for the conductivity at high temperatures, which is in agreement with the well-known experimental results. Similarly, m at low temperatures tends to 4 for transverse phonons and 3 for longitudinal phonons. This is in agreement with the theoretical results of Herring for the three-phonon-scattering relaxation rate at low temperatures. It has been further suggested in the present work that one can obtain the values of $m(T)$ quite conveniently by

$$m(T) = m_{av}(T) + G = m_{av}(T) + \ln(1+\Theta/\alpha T)/\ln T,$$

where Θ is the Debye temperature and α is the constant characteristic of the material. $m_{av}(T)$ is the average value of the upper and lower bounds of $m(T)$ obtained for Ge from the dispersion curves with the help of Guthrie's expressions. Previous workers gave discrete values to m, such as $m = 4$ for transverse phonons and $m = 3$ for longitudinal phonons at low temperature and further $m = 1$ for both the polarizations at high temperatures. Here m is taken to be the continuous function of the temperature as has been suggested by Guthrie. However, in the temperature range where isotopic scattering dominates over phonon-phonon scattering, the present relation for the temperature dependence of the three-phonon relaxation rate is not valid, as $e^{-\Theta/\alpha T}$ decreases very rapidly with temperature and one needs large values of m to compensate for the rapid decrease of the exponential factor.

Another significant feature of the present calculations is the use of Guthrie's classification of three-phonon scattering events. In class I events the carrier phonon is annihilated by combination and and in class II the annihilation takes place by splitting. Thus τ_{3ph}^{-1} is expressed as

$$\tau_{3ph}^{-1} = \tau_{3ph}^{-1}\ (\text{class I}) + \tau_{3ph}\ (\text{class II}).$$

For transverse phonons this leads to

$$[\tau_{3ph}^{-1}]_{Trans} = B_{T,I}\omega T^{m_{T,I}(T)} e^{-\Theta/\alpha T}$$

as only class I events are possible. For longitudinal phonons one obtains

$$[\tau_{3ph}^{-1}]_{Long} = B_{L,I}\omega^2 T^{m_{L,I}(T)} e^{-\Theta/\alpha T} + B_{L,II}\omega^2 T^{m_{L,II}(T)} e^{-\Theta/\alpha T}.$$

Another feature of the present approach is the use of the dispersion relation $\vec{q} = (\omega/\vec{v})(1+r\omega^2)$ to replace v_q/v_p^2 in the conductivity integrals. This gives

$$\frac{v_q}{v_p^2} = \frac{1}{v}\frac{(1+r\omega^2)^2}{(1+3r\omega^2)},$$

where r is given by $r=(1/\omega^2)(qv/\omega-1)$. The value of r is determined for the regions $\frac{1}{2}q_{max}$ to q_{max} and 0 to $\frac{1}{2}q_{max}$ from the dispersion curves.

In keeping with the ideas mentioned above, Hollands's formulation of two-mode conduction has been modified. Theoretical values of phonon conductivity are compared with Holland's experimental results in Ge. Good agreement has been obtained between theory and experiment for Ge in the entire temperature range 2–1000 °K.

The present approach is successful for those materials for which umklapp processes dominate over normal processes. Even if one used Callaway's model, one can show that the contribution due to three-phonon normal process is negligible in Ge. At high temperatures $\tau_u^{-1} > \tau_{pt}^{-1} + \tau_N^{-1}$, and at low temperatures $\tau_B^{-1} + \tau_{pt}^{-1} + \tau_u^{-1} > \tau_N^{-1}$, with the result that only umklapp processes made effective contribution toward thermal resistance.

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