

Calculations of anharmonic phonon relaxation times

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Abstract. Anharmonic phonon relaxation times in Ge are calculated using (i) an isotropic continuum model, and (ii) a dispersive model. A complete spectrum of calculated results is presented. Frequency-averaged values for normal- and umklapp-three-phonon relaxation times are also calculated. A comparison is made between our findings and some earlier works, and disagreements are discussed. The results are applied in calculating some results in the theory of lattice thermal conductivity.

Keywords. Anharmonicity; lattice thermal conductivity; phonon relaxation.

1. Introduction

In a previous paper (Srivastava 1974—referred to as S1 hereafter) it is mentioned that anharmonic phonon interactions are not amenable to a relaxation time picture (*see* also Parrott and Stuckes 1975), the basic reason being that such interactions are inelastic in nature. But for simplicity of understanding the problem one defines (Klemens 1951; Roufosse and Klemens 1973) an effective relaxation time τ_q (eff) for each phonon mode \vec{q} ($\equiv q, s$) by writing $(dN/dt)_{\text{int.}} \simeq -(N - \bar{N})/\tau$ (eff), where the left hand side gives the rate of change of the phonon distribution N over equilibrium \bar{N} due to interactions. Visualizing such a relaxation time picture is very difficult. Recent works prove it (*see* Hamilton 1973; Simons 1975). To make a useful relaxation time picture one talks of what is called the “single-mode relaxation time approximation.”

In the single-mode relaxation time picture one calculates the relaxation rate of phonons in a mode q , say, on the assumption that all other phonon modes have their equilibrium number (Klemens 1951; Carruthers 1961; Roufosse and Klemens 1973; Srivastava 1974; and Parrott and Stuckes 1975). This simplifying assumption gets only a little physical support in the review article by Carruthers (1961), who explains that the single-mode relaxation time picture gives essentially the ‘true’ relaxation time for low-frequency longitudinal phonons, and this too in the temperature range above the maximum in the conductivity versus temperature curve for a reasonably pure crystal. Otherwise, this picture, in theory, is not correct. The works by Callaway (1959), Hamilton (1973), and Simons (1975) show, however, that one can make corrections to this picture.

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In S1 we have derived expressions for three-phonon single-mode relaxation times τ_q for an isotropic continuum model. These results remove the earlier arbitrariness [e.g. Callaway 1959; Sharma *et al* 1971 (and references therein)] in the three-phonon coupling parameters by formulating explicit expressions for τ_q in terms of measurable quantities. Because of computing difficulties it was not possible to present any results in S1. In this paper we reformulate the expressions for single-mode three-phonon relaxation time for (i) an isotropic continuum model, and (ii) a dispersive model of the form of Born and von-Kármán, with a Debye cut-off scheme.

From the results of the present calculations we discuss the following points: (a) role of low-frequency phonon modes, (b) spontaneous decay of high-frequency longitudinal phonons, (c) relative importance of 'induced' and 'decay' processes, (d) relative importance of N - and U - processes, (e) energy surfaces for three-phonon scattering, (f) the spectrum of inverse relaxation times for both polarizations, (g) frequency-averaged inverse relaxation times, and (h) effect of dispersion on (f) and (g).

We also evaluate the effect of the correction term, due to Callaway, over the single mode relaxation rate. It is concluded that the effect is to give rise to a 'normal-drift', which is an important positive correction term to the conductivity of a pure crystal.

2. Single-mode relaxation times

From the previous work (S1) we write the result for single-mode relaxation time of phonons in mode q undergoing three-phonon processes of type $q + q' \rightleftharpoons (-q'')$ (called class I events) and $q \rightleftharpoons (-q') + (-q'')$ (called class II events):

$$\tau_q^{-1} = \frac{1}{2} \sum_{q', q''} \left[Q_{qq' q''} \frac{2\bar{N}'(\bar{N}'' + 1)}{(\bar{N} + 1)} \delta(\omega + \omega' - \omega'') \right. \\ \left. + \frac{\bar{N}'\bar{N}''}{\bar{N}} \delta(\omega - \omega' - \omega'') \right] \quad (1)$$

Here ω 's are phonon frequencies, \bar{N} 's are phonon equilibrium (Planck) distributions, and $Q_{qq' q''}$ are related to equilibrium transition rates for the three-phonon processes. The first and second terms in eq. (1) are the contributions from class I and class II events respectively.

To derive an expression for $Q_{qq' q''}$ we start with writing the crystal Hamiltonian up to third order anharmonic terms:

$$H = H_0 + \lambda H_{pp},$$

where

$$H_0 = \sum_q \hbar \omega_q a_q a_q^\dagger$$

and

$$H_{pp} = \frac{1}{3!} \sum_{q, q', q''} (a_q - a_{-q}^\dagger) (a_{q'} - a_{-q'}^\dagger) (a_{q''} - a_{-q''}^\dagger) \\ \times \mathcal{F}_{qq' q''} \delta(\vec{q} + \vec{q}' + \vec{q}'', \vec{G}) \quad (2)$$

and λ is a parameter deciding the order of perturbation H_{pp} over H_0 . Here a_q and $a_{\pm q}^{\pm}$ are, respectively, phonon annihilation and creation operators, \vec{G} is a reciprocal lattice vector, and $\mathcal{F}_{aa'q''}$ is a known positive function of q , q' and q'' . Following Leibfried and Schlömann (1954) we write

$$\mathcal{F}_{aa'q''} = \sqrt{5\hbar^3/(12\rho^3 N_0\Omega)} \frac{2\rho(\gamma + \frac{1}{2})}{a\omega_D} \sqrt{\omega\omega'\omega''} \quad (3)$$

where ρ is mass density, $N_0\Omega$ is volume of the crystal, γ is the Grüneisen constant, a is lattice constant, and ω_D is the Debye frequency. Leibfried and Schlömann's original formula for $|\mathcal{F}_{aa'q''}|^2$ contains γ^2 instead of $(\gamma + \frac{1}{2})^2$, which is a correction due to Steigmeir and Kudman (1966).

From the time-dependent perturbation theory in von-Hove's limit of weak-coupling ($\lambda^2 t \rightarrow 0$ as $t \rightarrow \infty$), the result for the transition probability

$$P(i, j) = 2\pi/\hbar |H_{pp}(E_i; E_j)|^2 N(E) \quad (4)$$

in the case of three-phonon processes after using eqs (2) and (3) (see S1), it becomes,

Class I events:

$$P_{aa'}^{a''} = Q_{aa'q''} NN' (N'' + 1) \delta(\omega + \omega' - \omega'') \quad (5)$$

Class II events:

$$P_a^{a'a''} = Q_{aa'q''} (N + 1) N' N'' \delta(\omega - \omega' - \omega'') \quad (6)$$

with

$$Q_{aa'q''} = \frac{10\pi\hbar(\gamma + \frac{1}{2})^2}{3N_0\Omega\rho a^2 \omega_D^2} \omega\omega'\omega'' \delta(\vec{q} + \vec{q}' + \vec{q}'', \vec{G}) \quad (7)$$

As done in S1 we convert the summations in eq. (1) in the light of momentum and energy conservation conditions, adopting the grafting scheme of Parrott (1963) to include U -processes in an isotropic continuum model with a Debye cut-off for wave vectors. The results are

$$\begin{aligned} \tau_a^{-1}(\text{cl. I}) &= \frac{5\hbar q_D^5 (\gamma + \frac{1}{2})^2}{6\pi\rho a^2 \omega_D^2} \sum_{\substack{s' s'' \\ \epsilon}} 1/c_{s''} \int dx' \frac{x'}{x} \\ &\quad \times WW' W'' (Cx + Dx') [1 - \epsilon + \epsilon(Cx + Dx')] \\ &\quad \times \frac{\bar{N}' (\bar{N}'' (Cx + Dx') + 1)}{(\bar{N} + 1)} \end{aligned} \quad (8)$$

$$\begin{aligned} \tau_a^{-1}(\text{cl. II}) &= \frac{5\hbar q_D^5 (\gamma + \frac{1}{2})^2}{12\pi\rho a^2 \omega_D^2} \sum_{\substack{s' s'' \\ \epsilon}} 1/c_{s''} \int dx' \frac{x'}{x} \\ &\quad \times WW' W'' (Cx - Dx') [1 - \epsilon + \epsilon(Cx - Dx')] \\ &\quad \times \frac{\bar{N}' \bar{N}'' (Cx - Dx')}{\bar{N}} \end{aligned} \quad (9)$$

Here $W = \omega/q_D$, etc., $C = c_s/c_{s'}$, $D = c_{s'}/c_{s''}$, and $\epsilon = 1$ and -1 for N- and U-processes respectively. For the continuum model $W = W_s = xc_s$, where x is

the reduced wave vector, $x = q/q_D$. For a dispersive model in the spirit of Born and von-Kármán, and in the approach of S1 for the energy surfaces, we can modify the frequencies by multiplying the results of the continuum model by the dispersion factor of a linear chain:

$$W_s = (2/\pi) c_s \sin(\pi x/2).$$

This clearly is not the full use of a dispersive model here. We are restricting ourselves to the Debye cut-off scheme, *i.e.*, to a spherical Brillouin zone. Because of this restriction we make use of the limits for x' in both the continuum and dispersive models as given in S1. Areas of integration in the $(x-x')$ space for different allowed three-phonon processes are shown in figure 1.

We can average τ_a^{-1} over frequency dependences for both N- and U-processes:

$$\langle \tau_y^{-1} \rangle = \frac{\sum_q C_{ph}(q) \tau_a^{-1}(y)}{\sum_q C_{ph}(q)} = \frac{\sum_q \omega_q^2 \tau_a^{-1}(y) \bar{N}(\bar{N} + 1)}{\sum_q \omega_q^2 \bar{N}(\bar{N} + 1)}$$

$$= \frac{\sum_s \int_0^1 dx x^2 W_s^2 \bar{N}_s(\bar{N}_s + 1) \tau_a^{-1}(y)}{\sum_s \int_0^1 dx x^2 W_s^2 \bar{N}_s(\bar{N}_s + 1)} \quad (10)$$

Here 'y' denotes N- or U-processes, and $C_{ph}(q)$ is specific heat for phonons in mode q .

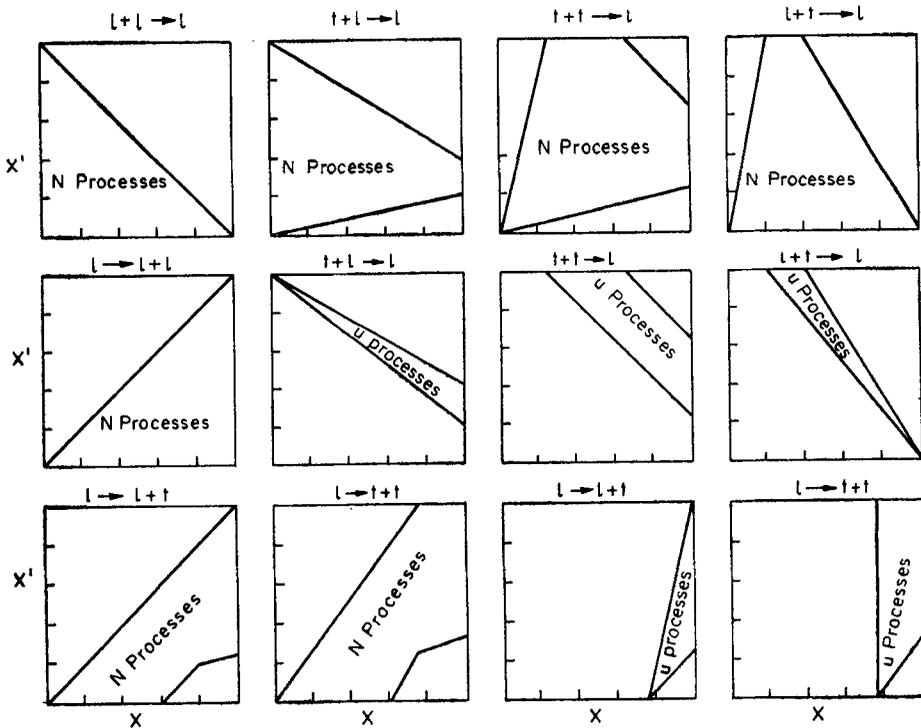


Figure 1. Integration domains for class I and class II three-phonon scattering events in the isotropic continuum model.

3. Approximate results for τ_q^{-1}

In this section we obtain approximate results for τ_q^{-1} in the low and high temperature regions. Going to the high temperature approximation $\bar{N} \simeq kT/(\hbar q_D c_s)$, etc. we obtain from eqs (8) and (9) for the continuum model

$$\tau_s^{-1}(s + s' \rightleftharpoons s'') = \frac{A}{G} \frac{\alpha^2}{\alpha'} x [(1 - \epsilon + \epsilon Cx) \frac{1}{2} f(x^2) + \epsilon D (1/3) g(x^3)] \quad (11)$$

and

$$\tau_s^{-1}(s \rightleftharpoons s' + s'') = \frac{A}{2G} \frac{\alpha^2}{\alpha'} x [(1 - \epsilon + \epsilon Cx) \frac{1}{2} f(x^2) - \epsilon D (1/3) g(x^3)] \quad (12)$$

where

$$A = \frac{5\hbar c_1^2 (\gamma + \frac{1}{2})^2 q_D^5}{6\pi \rho a^2 \omega_D^2}, \quad G = \hbar c_1 q_D / kT,$$

$\alpha = c_s/c_1$, $\alpha' = c_s'/c_1$, and $f(x^2)$ and $g(x^3)$ are functions of x^2 and x^3 respectively which are decided from integration domains for different allowed three-phonon processes.

At low temperatures ($\hbar\omega/kT > 1$) we approximate $\bar{N} \simeq \exp(-G \alpha x)$, etc., With this we get

$$\begin{aligned} \tau_{s,N}^{-1}(s \rightleftharpoons s' + s'') \\ = (A/2) \alpha \alpha' [C^2 x^2 (1/3) g(x^3) - 2CDx (1/4) h(x^4) + D^2 (1/5) o(x^5)] \end{aligned} \quad (13)$$

with $g(x^3)$, $h(x^4)$ and $o(x^5)$ as appropriate functions of x^3 , x^4 , and x^5 respectively, which are decided from integration domains of class II type of N -processes.

Also, going to a very low temperature region we approximate

$$\begin{aligned} \tau_{s,N}^{-1}(s + s' \rightleftharpoons s'') \\ = A \alpha \alpha' [\alpha^2 x^2 \int dx' x'^2 \exp(-a' Gx') \\ + 2\alpha \alpha' x \int dx' x'^3 \exp(-a' Gx') + \alpha'^2 \int dx' x'^4 \exp(-a' Gx')] \\ \cong (A/G) \frac{\alpha}{\alpha'^2} [\alpha^2 3! \zeta(3) x^2 + 2\alpha 4! \zeta(4) x/G + 5! \zeta(5)/G^2] \end{aligned} \quad (14)$$

where we use

$$\begin{aligned} \int dx' x'^n \exp(-tx') &\simeq \int_0^{\infty} dx' x'^n \exp(-tx') \\ &= t^{-(n+1)} (n+1)! \zeta(n+1), \end{aligned}$$

ζ being Reimann zeta function.

To discuss low temperature results for U-processes we write

$$\begin{aligned} \tau_{s,U}^{-1}(s + s' \rightleftharpoons s'') = A \alpha \alpha' \int_{x'_{\min}} dx' x'^2 (Cx + Dx') (2 - Cx - Dx') \\ \exp(-a' Gx') \end{aligned}$$

where x'_{\min} is the minimum value of x' for an U-process to start which may or may not be zero depending upon the combinations of s , s' and s'' . To handle such an integral we proceed as follows (see e.g., Srivastava and Verma 1971):

$$\begin{aligned}
\int_{x'_{\min}} dx' x'^n \exp(-tx') &= \exp(-tx'_{\min}) \int d(x' - x'_{\min}) (x' - x'_{\min})^n \\
&\quad \times \exp[-t(x' - x'_{\min})] \\
&= \exp(-tx'_{\min}) \int_0^\infty dz z^n \exp(-tz) \\
&\simeq \exp(-tx'_{\min}) (n+1)! \zeta(n+1) t^{-(n+1)}.
\end{aligned}$$

This gives

$$\begin{aligned}
\tau_{s,U}^{-1}(s + s' \rightleftharpoons s'') &= (A/G^3) \exp(-a'Gx'_{\min}) (a/a')^3 [Cx(2 - Cx) 3! \zeta(3) \\
&\quad + 2D(1 - Cx) 4! \zeta(4) 1/(a'G) - D^2 5! \zeta(5) 1/(a'^2 G^2)] \quad (15)
\end{aligned}$$

It can be noticed from figure 1 that $x'_{\min} = 0$ for U-processes of the type $1 + t \rightleftharpoons 1$, but $x'_{\min} = (1 - c_i/c_1)/(1 + c_i/c_1)$ for $t + t \rightleftharpoons 1$, and $x'_{\min} = (1 - c_i/c_1)/2$ for $t + 1 \rightleftharpoons 1$.

For class II type U-processes there is a special restriction. These cannot occur for, say $x < 2/(1 + c_1/c_2) = x_0$. Also, in the continuum model class II events occur for carrier phonons with longitudinal modes only. Therefore for x greater than x_0 we must have $\hbar\omega_1/kT = \Theta_{1x}/T \geq \Theta_{1x_0}/T \cong \Theta_D/T$, which for $T < \Theta_D$ is greater than unity. (Note that Θ_D is an averaged Debye temperature, whereas Θ_1 is the Debye temperature corresponding to longitudinal modes). This means that for $T \geq \Theta_D$ U-processes of class II type can occur for high frequency phonons ($\hbar\omega > kT$) only. For such phonons we have below the Debye temperature

$$\begin{aligned}
\tau_{s,U}^{-1}(s \rightleftharpoons s' + s'') &= (A/2) aa' \int dx' x'^2 (Cx - Dx') (2 - Cx + Dx') \\
&\simeq (A/2) aa' [Cx(2 - Cx) \cdot (1/3) g(x^3) \\
&\quad + 2D(Cx - 2) \cdot (1/4) \cdot h(x^4) - D^2 \cdot (1/5) \cdot o(x^5)]. \quad (16)
\end{aligned}$$

Assuming that the bracketed terms in eqs (13) and (16) are nearly equal to each other we are left with the result that $\tau_{s,N}^{-1} \simeq \tau_{s,U}^{-1}$ for high-frequency phonons at low temperatures.

The findings in eqs (11-16) have already been discussed in S1. But here we have given explicit expression in terms of measurable quantities. The functions $f(x^2)$, $g(x^3)$, $h(x^4)$ and $o(x^5)$ are not difficult to obtain: they are to be decided from integration domains in figure 1 for different three-phonon processes.

4. Discussion of results

a. Role of low-frequency modes

Herring (1954) and Klemens (1956, 1958, 1969) have discussed the frequency dependence of N -process relaxation rates of low-frequency phonon modes. In this section we see how we get their findings. We also compare our few particular results with those due to Klemens and discuss the results.

Herring's work shows that for $q \rightarrow 0$ at any temperature T

$$\begin{aligned}
\tau_{s,N}^{-1}(s + s' \rightleftharpoons s'') \Big|_{q \rightarrow 0} &\propto q^n \quad n = 1, 2, 5/2, 3 \text{ or } 4 \\
&\quad (5/2 \text{ at high } T \text{ only})
\end{aligned}$$

$$\begin{aligned} \tau_{s,N}^{-1} (s + s' \rightleftharpoons s'') \mid q' \sim q &\propto q^4 \\ \tau_{s,N}^{-1} (s \rightleftharpoons s' + s'') &\propto q^4 \end{aligned} \quad (17)$$

Klemens finds for $q \rightarrow 0$

$$\begin{aligned} \tau_{t,N}^{-1} (t + 1 \rightleftharpoons 1) &a q \\ \tau_{1,N}^{-1} (1 \rightleftharpoons t + t) &a q^4. \end{aligned} \quad (18)$$

Clearly Klemens' findings are included in those of Herring's. The first process in eq. (18) is called Landau-Rumer (1937) process.

Let us first consider class II type of events. From figure 1 we note that for all N -processes of type II, the x' curve passes through the origin: $x' = x(C + 1)/(D + 1)$. Therefore for $q \rightarrow 0$ this gives in eq. (12)

$$f(x^2) = x'^2 \mid_a^b(x), \quad g(x^3) = x'^3 \mid_a^b(x),$$

with $a(x) = 0$ and $b(x) = x(C + 1)/(D + 1)$, so that we get

$$f(x^2) = x^2 ((C + 1)/(D + 1))^2, \quad \text{and} \quad g(x^3) = x^3 ((C + 1)/(D + 1))^3.$$

Thus from eq. (12)

$$\tau_{s,N}^{-1} (s \rightleftharpoons s' + s'') \propto q^4 \quad \text{low } q \text{ high } T$$

which is the case in eqs (17) and (18).

In section 3 we have not considered the behaviour of N -processes of type II when $q \rightarrow 0$; what eq. (13) considers is the case at low temperatures when $\hbar\omega > kT$, i.e., it is the result for high-frequency phonons. The case at low temperatures for $q \rightarrow 0$ is very tricky. We handle it by considering the form

$$\begin{aligned} \tau_{s,N}^{-1} (s \rightleftharpoons s' + s'') &\propto \int dx' \frac{x'}{x} W W' W'' x'' \bar{N}' \bar{N}'' / \bar{N} \\ &\propto \int dx' x'^2 x''^2. \end{aligned}$$

For decay processes with very small q we take $x \cong 1x' \cong mx''$, $1, m > 1$. This gives

$$\tau_{s,N}^{-1} (s \rightleftharpoons s' + s'') \propto x^4 \int dx'.$$

Now the integral $\int dx'$ will limit the contributions to only the portion of dx' for which $\hbar\omega' \simeq nkT$, $n \leq 1$; so we would expect $\int dx' \propto T$. This therefore gives for $q \rightarrow 0$

$$\tau_{s,N}^{-1} (s \rightleftharpoons s' + s'') \propto q^4 T \quad \text{low } T \quad (13')$$

which is consistent with the findings in eqs (17) and (18).

For class I events with low q we have from figure 1 the following results.

$$\left. \begin{aligned} t + t \rightleftharpoons 1 \\ 1 + t \rightleftharpoons 1 \end{aligned} \right\} \text{(where } q' \sim q): f(x^2) \propto x^2, g(x^3) \propto ax^3, \text{ and } h(x^4) \propto ax^4,$$

$$\left. \begin{aligned} t + 1 \rightleftharpoons 1 \\ 1 + 1 \rightleftharpoons 1 \end{aligned} \right\} \text{(where } q' > q): f(x^2), g(x^3), h(x^4) \propto x^0.$$

With these results in mind we get from eq. (11)

$$\begin{aligned}\tau_{s,N}^{-1}(s + s' \rightleftharpoons s'')|_{q' > a} &\propto q^n, \quad n = 1, 2 & q \rightarrow 0 \quad \text{high } T \\ \tau_{s,N}^{-1}(s + s' \rightleftharpoons s'')|_{q' \sim a} &\propto q^4.\end{aligned}$$

These findings are the predictions of Herring and Klemens. However, with this simplified picture we are not able to get $q^{5/2}$ dependence at high temperatures, which is obtained in Herring's analysis. Further at very low temperatures we get from eq. (14)

$$\tau_{s,N}^{-1}(s + s' \rightleftharpoons s'') \propto q^n, \quad n = 0, 1, 2.$$

We can say that at very low temperatures this prediction is correct and is included in the findings of Herring and Klemens if we assume that at these temperatures only N-processes of type $t + 1 \rightleftharpoons 1$ and $1 + 1 \rightleftharpoons 1$ exist, and only those for which $f(x^2)$, $g(x^3)$, $h(x^4) \propto x^0$.

Klemens (1956, 1958, 1969) has estimated the inverse relaxation times τ_N^{-1} for both longitudinal and transverse phonons of low frequency. However, these estimates, are not consistent, as can be gathered from his three articles referred to above. Also, it is not very clear what combination of various class I and class II events he has considered in making these estimates. Although his article in 1969 gives a more recent version of the results, it does not give full details as compared to his article in 1958. Therefore we consider his results as given in *Solid State Physics*, Vol. 7 (1958) where the processes $1 \rightleftharpoons t + t$ and $1 \rightleftharpoons 1 + t$ are considered in evaluating $\tau_{1,N}^{-1}$ (first treated by Pomeranchuk 1942); and the process $t + 1 \rightleftharpoons 1$ in evaluating $\tau_{t,N}^{-1}$. His estimates for $q \rightarrow 0$ are

$$\tau_{t,N}^{-1} = \tau_{t,N}^{-1}(t + 1 \rightleftharpoons 1) = (100/6\pi)\gamma^2 (kT/Mv^2) (v/a) (aq) (akT/\hbar v)^3 \quad (18')$$

$$\tau_{1,N}^{-1} = (16/3\pi)\gamma^2 (aq)^4 (v/a) (kT/Mv^2), \quad (18'')$$

where $M = \rho a^3$ and $v = c_s$ in our notations.

It would be desirable to compare these results with ours. At very low temperatures ($T \leq \Theta_D$) our result in eq. (14) becomes

$$\begin{aligned}\tau_{t,N}^{-1}(t + 1 \rightleftharpoons 1) &= 1.29 \times 10^{-12} q^2 T^3 [1 + 3.6 \times 10^{-3} (T/x) \\ &+ 4.31 \times 10^{-4} (T/x)^2].\end{aligned} \quad (14')$$

It can be seen from eq. (14') that if $T \leq x (\leq 1)$ we can neglect the second and third terms in the same. $T \leq x$ corresponds to $T \leq 1^\circ K$. But for $x \leq T \leq \Theta_D$ we have to retain the second and third terms. Keeping to low temperature region we would expect the second term to be important (see also Eng 1969) for the Landau-Rumer process $t + 1 \rightleftharpoons 1$. With this consideration we write our result, eq. (14'), as below

$$\tau_{t,N}^{-1}(t + 1 \rightleftharpoons 1)|_{GP} = 1.29 \times 4.97 \times 10^{-6} qT^4 \quad (14'')$$

$$= 2.05 \times 10^{-11} \cdot \omega T^4 \quad (14''')$$

while Klemens' result, eq. (18), is

$$\tau_{t,N}^{-1} (t + 1 \rightleftharpoons 1) |_{\text{Klem}} = 2.85 \cdot 10^{-10} \omega T^4 \quad (18''')$$

Jackson and Walker (1971) who also studied the problem find and from their curve fitting procedure in NaF that the best fit between 10 and 25° K to the thermal conductivity measurements and the second-sound observations require the following result

$$\tau_{N}^{-1} |_{\text{JW}} = 1 \times 10^{-10} \omega T^4 \quad (19)$$

We find from eqs (14''') and (18''') that Klemens' estimate of $\tau_{t,N}^{-1}$ for low-frequency modes is about 7 times higher than ours. Since Jackson and Walker have not clearly studied the distinct contribution due to $t + 1 \rightleftharpoons 1$ N -process (at low temperatures for $q \rightarrow 0$ contribution due to $1 + 1 \rightleftharpoons 1$ will probably be equally important and hence deserves consideration), we are unable to compare their result, eq. (19), with ours. Secondly, their procedure will lead in Ge to a numerical factor different from that in eq. (19). However, the results in eqs (14'''), (18') and (19) are within acceptable limits of one another.

To compare Klemens' estimate of $\tau_{1,N}^{-1}$ for low-frequency longitudinal modes we consider our results in eq. (12). To make a reasonable comparison with Klemens' we consider only the processes $1 \rightleftharpoons t + t$ and $1 \rightleftharpoons 1 + t$ in estimating $\tau_{1,N}^{-1}$. At a high temperature T eq. (12) yields, for $q \rightarrow 0$,

$$\begin{aligned} \tau_{1,N}^{-1} |_{\text{GP}} &= 4\tau_{1,N}^{-1} (1 \rightleftharpoons t + t) + 4\tau_{1,N}^{-1} (1 \rightleftharpoons 1 + t) \\ &= 1 \cdot 16 \times 10^{-46} \omega_1^4 T, \end{aligned} \quad (12')$$

whereas eq. (18''') gives

$$\tau_{1,N}^{-1} |_{\text{Klem}} = 4 \cdot 16 \cdot 10^{-45} \omega_1^4 T \quad (18'')$$

Eqs (12') and (18'') suggest that Klemens' estimate of $\tau_{1,N}^{-1} (q \rightarrow 0)$ is about 36 times higher than such an estimate made in the present work.

Thus we find that Klemens' estimates of inverse relaxation times for low-frequency phonon modes are in general higher than those obtained in the present paper. We explain this disagreement by saying that Klemens' choice for the anharmonic Hamiltonian, together with various approximations used by him in summing over polarization branches and wave vectors, may be wrong. The first of these points is supported by Parrott and Stuckes (1975) (page 114, foot note), who observe that the transition probabilities used by Klemens (and subsequently by Roufosse and Klemens 1973) are sixteen times greater than the generally accepted ones. The disagreements caused by summation procedures over polarization branches may be a matter of controversy (see the disagreement between Klemens' estimates in 1956 and 1958). Finally the error caused by the approximation used by Klemens in converting summations over wave vectors into integral forms is also responsible for a part of the above disagreement.

b. Spontaneous decay of high-frequency longitudinal phonons

The question of anharmonic decay of high-frequency longitudinal phonons at low temperatures is discussed in detail by Klemens (1967). At low temperatures such that $\hbar\omega > kT$, we find from eq. (13) that $\tau_{1,N}^{-1} (1 \rightleftharpoons s' + s'') \propto q^5$. This means

decay of high-frequency longitudinal phonons at any low temperatures (such that $\hbar\omega > kT$) is spontaneous. This comes true from Klemens' theory, and also from the work of Benin (1970) in the theory of lattice thermal conductivity. For a high frequency longitudinal phonon to decay, at a low temperature, into two other of lower frequencies does not initially require the presence of any other phonons.

Klemens' calculation of spontaneous decay rates of such phonons is essentially based upon perturbation theory, which is also used in our calculations. But Klemens has used further approximations in his calculations and we have not. We compare here Klemens approximate calculations with our schematic ones. Klemens obtains the total attenuation in the form

$$\tau_N^{-1} = (3\pi/4 \sqrt{2}) \gamma^2 \omega (\hbar\omega/Mv^2) (\omega/\omega_D)^3 (v_1/v_{II}) [1 + 4kT/\hbar\omega + F(T)] \quad (20)$$

The temperature independent term is the spontaneous decay rate which we write after recognizing $M = \rho a^3$, $v_1 = c_1$, and $v_{II} = c_t$,

$$\begin{aligned} \tau_{1,N}^{-1} &= 2\tau_{1,N}^{-1} (1 \Rightarrow 1 + t) + 4\tau_{1,N}^{-1} (1 \Rightarrow t + t) \\ &= [3\pi\gamma^2 \hbar/(4 \sqrt{2}\rho c_1 c_t a^3 \omega_D^3)] \cdot \omega^5. \end{aligned} \quad (21)$$

Here the factors 2 and 4 with the processes $1 \Rightarrow 1 + t$ and $1 \Rightarrow t + t$ respectively are as considered by Klemens due to summation over the polarizations s' and s'' in the result $\tau_s^{-1} = \sum_{s's''} \tau_s^{-1} (s \Rightarrow s' + s'')$.

Our results from eq. (13) are (see S1)

$$\begin{aligned} \tau_{1,N}^{-1} &= \tau_{1,N}^{-1} (1 \Rightarrow 1 + 1) + 4\tau_{1,N}^{-1} (1 \Rightarrow 1 + t) + 4\tau_{1,N}^{-1} (1 \Rightarrow t + t) \\ &= [5\hbar c_1^2 (\gamma + \frac{1}{2})^2 q_D^5 / (12\pi\rho a^2 \omega_D^2)] \cdot \\ &\quad \times x^5 [1/30 + (4/5) (c_1/c_t)^2 + 4c_1/c_t \cdot (1/3) (c_1/c_t)^2 ((c_1/c_t + 1)/2)^3 \\ &\quad - (1/2) (c_1/c_t) [(c_1/c_t + 1)/2]^4 + (1/5) [(c_1/c_t + 1)/2]^5]. \end{aligned}$$

In order to compare our results with that of Klemens it would be fair to take γ^2 instead of $(\gamma + \frac{1}{2})^2$. Further, taking $c_1/c_t = 1.6$ for the continuum model the above equation becomes

$$\tau_{1,N}^{-1} |_{GP} = 5.88 \hbar \gamma^2 \omega^5 / (12\pi\rho a^2 \omega_D^2 c_1^3). \quad (22)$$

A comparison of results (21) and (22) gives

$$\tau_{1,N}^{-1} (GP) / \tau_{1,N}^{-1} (\text{Klem}) = 5.88 \sqrt{2} a \omega_D c_t / (9\pi^2 c_1^2),$$

which for $\omega_D = c_1 q_D$ gives

$$\begin{aligned} \tau_{1,N}^{-1} (GP) / \tau_{1,N}^{-1} (\text{Klem}) &= 5.88 \sqrt{2} a q_D / 9\pi^2 \quad (23) \\ &= 0.42. \quad (23') \end{aligned}$$

This shows that our finding (presumably the correct result) for the spontaneous decay rate is less than half of that obtained by Klemens. We reiterate that the reason for this difference by a factor of more than two lies in the various approximations used by Klemens in evaluating the summations over phonon modes (wave vectors and polarizations), and in considering a rather wrong Hamiltonian.

(c) *Relative importance of class I and class II events*

Separate consideration of class I and class II three-phonon events has been taken into account recently by Sharma *et al* (1971) in calculating lattice thermal conductivity by using single-mode relaxation time method. But their treatment is based purely on qualitative considerations and lacks any quantitative arguments. In general one should expect low-frequency modes to have higher inverse relaxation times for class I events than for class II events. At low temperatures, where most phonons are in the low-frequency range, we expect by virtue of the above assertion that τ_s^{-1} (cl. I) $>$ τ_s^{-1} (cl. II). With the increase of temperature, phonons get excited towards the high frequency range, and then we expect class II events to yield higher contributions to inverse relaxation times than class I events. Our calculations show that at all temperatures when $x \geq 0.8$, then τ_s^{-1} (cl. II) $>$ τ_s^{-1} (cl. I), and when $x < 0.8$, then τ_s^{-1} (cl. I) $>$ τ_s^{-1} (cl. II).

(d) *Energy surfaces for three-phonon processes*

We have used an isotropic continuum model in drawing the areas in the $(x - x')$ space for different three-phonon processes. These areas are decided by simultaneous consideration of energy and momentum conservation. We find from figure 1 that the areas for various allowed processes are different. The surfaces of revolutions of these areas about the x -lines are the surfaces of energy conservation for various allowed events. As can be imagined the energy surfaces thus obtained will be quite complicated in most cases. A general picture of such surfaces for class I N -processes has been sketched by Ziman (1966). For class II N -processes the same is done by Klemens (1967). One can of course draw these surfaces for different N - and U -processes and it would appear that the pictures presented by Ziman and Klemens are just illustrative and the real surfaces due to a model would in general be quite complicated for both N - and U -processes. Use of a dispersive model will modify these areas in the $(x - x')$ space, and hence the shapes of these energy surfaces in general.

(e) *Relative importance of N - and U -processes*

$t + 1 \rightleftharpoons 1$ is the only kind of event for which U -processes can start even for quite low q ; otherwise as discussed in section 3 there is a minimum value of q below which U -processes do not start at all. When q becomes quite large enough then U -processes become more numerous. At high temperatures one expects phonons to have high q values, and therefore one can expect contributions from U -processes to become as equal to or even more than that from N -processes. At low temperatures spontaneous U -decay of high frequency phonons may not be as strong as spontaneous N -decay. Our calculations show that (i) at high temperatures when $x \geq 0.8$, $\tau_{s,U}^{-1} > \tau_{s,N}^{-1}$, and when $x < 0.8$, $\tau_{s,N}^{-1} > \tau_{s,U}^{-1}$; and (ii) at low temperatures when $x \geq 0.8$, $\tau_{1,N}^{-1} \approx \tau_{1,U}^{-1}$ and when $x < 0.8$, $\tau_{1,N}^{-1} > \tau_{1,U}^{-1}$, and when $x \geq 0.97$, $\tau_{t,N}^{-1} \approx \tau_{t,U}^{-1}$ and when $x < 0.97$, $\tau_{t,N}^{-1} > \tau_{t,U}^{-1}$. These findings suggest that at low temperatures spontaneous decay of high-frequency phonons near the zone boundary is equally due to U -processes and N -processes, and for phonons well within the zone the contribution from N -processes is higher. At high temperatures where we find the U -contribution larger than the N -contribution, we conclude that most phonons have large q values.

(f) Contributions from separate polarizations and the spectrum of inverse relaxation times

We find from our calculations for the isotropic continuum model that longitudinal phonons have higher inverse relaxation times than transverse phonons at all temperatures. For example, we have at 300° K, $\tau_t^{-1}/\tau_1^{-1} = 0.371$ for $x = 0.0053$ and $\tau_t^{-1}/\tau_1^{-1} = 0.046$ for $x = 0.995$, and at 10° K, $\tau_t^{-1}/\tau_1^{-1} = 0.370$ for $x = 0.0053$ and $\tau_t^{-1}/\tau_1^{-1} = 0.603 \cdot 10^{-6}$ for $x = 0.995$. These findings indicate that the conductivity due to longitudinal phonons should be much lower than that due to transverse phonons. Inclusion of dispersion alters these findings: at 300° K, $\tau_t^{-1}/\tau_1^{-1} = 0.373$ for $x = 0.0053$ and $\tau_t^{-1}/\tau_1^{-1} = 0.0524$ for $x = 0.995$, and at 10° K, $\tau_t^{-1}/\tau_1^{-1} = 0.369$ for $x = 0.0053$ and $\tau_t^{-1}/\tau_1^{-1} = 0.473 \cdot 10^{-6}$ for $x = 0.995$.

The present calculations give the following picture of the spectrum of inverse relaxation times (see table 1):

Both for the continuum and the dispersive models the smallest contribution to the inverse relaxation times comes from transverse modes with short wave vectors (*i.e.*, with $s = t$, $q \rightarrow 0$) in the whole temperature range 900–8° K. Below this temperature, say at 5° K and below, we obtain the minimum due to transverse modes with $x = 0.64$ rather than with $x \rightarrow 0$. Down to 8° K the result for the minimum from the dispersive model is somewhat higher than that from the continuum model (of course the difference between the two sets of results is not appreciable). But below 8° K the dispersive model yields higher results than does the continuum model. Probably for such low temperatures use of the dispersive

Table 1. Maximum and minimum of inverse relaxation times in Ge*
(unit: per sec.)

Temperature (°K)	Non-dispersive		Dispersive	
	$(\tau_a^{-1})_{\min}$	$(\tau_a^{-1})_{\max}$	$(\tau_a^{-1})_{\min}$	$(\tau_a^{-1})_{\max}$
900	0.6125 (9)	0.5750 (13)	0.6173 (9)	0.2272 (13)
700	0.4706 (9)	0.4490 (13)	0.4768 (9)	0.1753 (13)
350	0.2153 (9)	0.2313 (13)	0.2268 (9)	0.8491 (12)
300	0.1770 (9)	0.2010 (13)	0.1898 (9)	0.7210 (12)
100	0.2183 (8)	0.9146 (12)	0.3317 (8)	0.2230 (12)
60	0.4048 (7)	0.7750 (12)	0.7302 (7)	0.1333 (12)
40	0.8370 (6)	0.7331 (12)	0.1320 (7)	0.1238 (12)
30	0.2654 (6)	0.7201 (12)	0.3427 (6)	0.1224 (12)
10	0.3276 (4)	0.7072 (12)	0.3339 (4)	0.6963 (13)
5	0.1669 (2)	0.7063 (12)	0.1391 (2)	0.2178 (18)
4	0.4090	0.7062 (12)	0.3484	0.5088 (20)

* The figures in brackets represent exponent.

model in our spirit becomes inaccurate. However any inaccuracies at low temperatures will be swept over by the inclusion of boundary and defect scattering.

Contribution towards the largest inverse relaxation times comes from longitudinal modes of long wave vectors for both the continuum and dispersive models. In case of the continuum model we find that longitudinal modes near the zone boundary contribute towards the largest inverse relaxation time for all temperatures 900–4° K. But in our dispersive model (which is not a full dispersive model) we find that the maximum is contributed by longitudinal modes near the zone boundary down to 60° K, but below this temperature with $x = 0.8$. It should be mentioned here again that consequences of a more reasonable dispersive model could well be different from these findings either at high or low or at both temperatures. However, the dispersive effect in the present work is found to reduce the value of largest inverse relaxation time as compared to the continuum model down to 14° K, and to increase the same below this temperature. This increase below 14° K may be due to the misuse or incomplete use of dispersion in our approach. However, as mentioned above the low temperature discrepancies are swept out by boundary and defect scattering rates.

For the continuum model we also find that $\tau_1^{-1} (q \sim q_D) \propto T$ at high temperatures, and $\tau_1^{-1} (q \sim q_D) \approx \text{constant}$ at low temperatures. We explain this by saying that the number of high-frequency phonons remains constant at low temperatures where they decay spontaneously (constant of temperature), but as the temperature increases higher the number of such phonons increases linearly with temperature and therefore their decay rate is proportional to T . These findings support the result used by Benin (1970) in developing his variational theory of lattice thermal conductivity.

(g) Average inverse relaxation times

In the previous sub-section we have discussed the whole spectrum of inverse relaxation times. If we average the results over frequency dependences, we can talk of the relative importance of N- and U-processes in different temperature ranges. Also, such averaged results may give some idea in making a choice of inverse relaxation times for N- and U-processes in the study of thermal conductivity. Further, such results may be helpful in studying essential conditions for second-sound propagation in a solid (*see e.g.*, Jackson and Walker 1971).

Table 2 gives our calculated results for $\langle \tau_N^{-1} \rangle$ and $\langle \tau_U^{-1} \rangle$ for both dispersive and non-dispersive models. In the non-dispersive case U-processes are found to be stronger than N-processes down to 200° K, but below this temperature N-processes become stronger than U-processes. In fact at very low temperatures N-processes become infinitely stronger than U-processes. For the dispersive model U-processes are somewhat stronger than N-processes down to 400° K, and below it N-processes take dominance. Dispersive results are in general lower than the nondispersive ones down to nearly 60° K, but higher below it. However, we find that this dispersion law does not affect the N-results much at low temperatures, whereas it affects the U-results very much. The conclusions arrived at here from the dispersive model may not be quite correct. This is probably because the

Table 2. Frequency-averaged results of N- and U-relaxation rates in Ge.*
(unit: per sec.)

Temperature (°K)	Present calculations						<i>JW</i> 's results for NaF ($\Theta_D=466^\circ\text{K}$)
	(Dispersive)			(Non-dispersive)			
	$\langle \tau_N^{-1} \rangle$	$\langle \tau_u^{-1} \rangle$	$\frac{\langle \tau_N^{-1} \rangle}{\langle \tau_u^{-1} \rangle}$	$\langle \tau_N^{-1} \rangle$	$\langle \tau_u^{-1} \rangle$	$\frac{\langle \tau_N^{-1} \rangle}{\langle \tau_u^{-1} \rangle}$	
900	0.271 (12)	0.273 (12)	0.994	0.496 (12)	0.548 (12)	0.903	..
700	0.209 (12)	0.210 (12)	0.995	0.384 (12)	0.424 (12)	0.905	..
500	0.147 (12)	0.148 (12)	0.997	0.271 (12)	0.299 (12)	0.907	..
300	0.846 (11)	0.843 (11)	0.100 (1)	0.156 (12)	0.170 (12)	0.917	..
100	0.198 (11)	0.187 (11)	0.106 (1)	0.312 (11)	0.298 (11)	0.105 (1)	0.103 (1)
60	0.683 (10)	0.581 (10)	0.117 (1)	0.805 (10)	0.570 (10)	0.141 (1)	0.151 (1)
40	0.194 (10)	0.135 (10)	0.144 (1)	0.167 (10)	0.576 (9)	0.289 (1)	0.304 (1)
30	0.590 (9)	0.302 (9)	0.195 (1)	0.434 (9)	0.454 (8)	0.956 (1)	0.692 (1)
20	0.741 (8)	0.135 (8)	0.549 (1)	0.581 (8)	0.167 (6)	0.349 (3)	0.425 (2)
15	0.155 (8)	0.555 (6)	0.279 (2)	0.138 (8)	0.408 (3)	0.338 (5)	0.293 (3)
10	0.189 (7)	0.924 (3)	0.204 (4)	0.182 (7)	0.137 (-2)	0.133 (10)	0.165 (5)
5	0.573 (5)	0.254 (-5)	0.226 (11)	0.568 (5)	0.114 (-19)	0.497 (25)	0.100 (10)
4	0.190 (5)	0.102 (-9)	0.187 (15)	0.189 (5)	.253 (-28)	0.748 (33)	0.312 (13)

* The figures in brackets represent exponent.

present dispersive approach does not modify the energy surfaces and density of states, which it ought to be. Non-dispersive results are, however, correct within the validity of the model.

We find that

$$\langle \tau_N^{-1} \rangle \propto T^5 \quad (24 a)$$

explains the low temperature behaviour, and

$$\langle \tau_U^{-1} \rangle \propto T^4 \exp(-\Theta_D/0.95T) \quad (24 b)$$

explains the low temperature behaviour of our calculated results in table 2. Jackson and Walker (1971) have obtained the following results for averaged inverse relaxation times in NaF

$$\left. \begin{aligned} \langle \tau_N^{-1} \rangle &= 60T^5 \\ \langle \tau_U^{-1} \rangle &= 2.2 \cdot 10^4 T^4 \exp(-\Theta_D/3.5T) \end{aligned} \right\} \quad (25)$$

Eq. (25) suggests that *JW*'s approach in *Ge* would lead to our findings of eq. (24) with the factor $\exp(-\Theta_D/0.95T)$ replaced by $\exp(-\Theta_D/\beta T)$ where β may be different from 0.95. As can be seen from table 2, where we also tabulate the ratio-

$\langle \tau_N^{-1} \rangle / \langle \tau_U^{-1} \rangle$ from eq. (25), both our and *JW*'s results show the behaviour $\langle \tau_N^{-1} \rangle > \langle \tau_U^{-1} \rangle$ at low temperatures. This is reasonable, because U-processes get frozen out as temperature decreases below a fraction of the Debye temperature, the behaviour which can also be studied from figure 1 if we remember that at quite low temperatures most phonons are in low-frequency range. However, the ratio $\langle \tau_N^{-1} \rangle / \langle \tau_U^{-1} \rangle$ from eq. (25) does not agree with that of eq. (24). For example at 10° K this ratio is about 10^9 , whereas from eq. (25) it comes about 10^4 . Assuming that the ratio $\langle \tau_N^{-1} \rangle / \langle \tau_U^{-1} \rangle$ should be nearly the same in all the cubic crystals, and further, presuming that *JW*'s choice for τ_N^{-1} is correct, we are left with the idea that their choice for τ_U^{-1} , viz., $\tau_U^{-1} = B_U \omega^2 T^2 \exp(-\Theta_D/\beta T)$, ($B_U = 4 \cdot 6 \cdot 10^{-20}$) is a very rough overestimate and should be modified, including a proper value for β and the coupling constant B_U which they regard as a parameter, such that it leads to a correct ratio of $\langle \tau_N^{-1} \rangle / \langle \tau_U^{-1} \rangle$ at low temperatures.

The high temperature forms used by *JW* are

$$\begin{aligned} \tau_N^{-1} &\propto \omega T \\ \tau_U^{-1} &\propto \omega^2 T / (\exp(z) - 1), \quad z = \hbar\omega/kT. \end{aligned} \quad (26)$$

The form for τ_N^{-1} is included in our findings [eq. (11)]. But their form for τ_U^{-1} can be expressed as

$$\begin{aligned} \tau_U^{-1} &\propto \omega^2 T / (\exp(z) - 1) \\ &\propto \omega T^2 \end{aligned} \quad (27)$$

where we approximate $\exp(z) \simeq 1 + z$. The T^2 dependence for τ_U^{-1} as observed in the choice of *JW* may not be favoured at high temperatures, where we expect T dependence for three-phonon resistance. Thus we conclude that *JW*'s choice for U-scattering rate will lead to a wrong temperature dependence for $\langle \tau_U^{-1} \rangle$ at high temperatures too.

5. Application of results in calculation of thermal conductivity

The single-mode relaxation time theory yields what is called the Debye term for the conductivity. One can calculate the Debye term by using the results obtained in section 2. However, we shall concentrate on calculating the results of invoking the role of the other modes over the single-mode theory. Callaway (1959) defined a combined relaxation time τ_C by $\tau_C = \tau (1 + \beta/\tau_N)$, where τ is the 'single-mode' relaxation time $\tau^{-1} = \tau_N^{-1} + \tau_U^{-1}$. The dimensionless parameter β represents the role of the N-processes, which can be obtained by trying to take account of all the modes and using the fact that momentum is conserved for such processes. In other words τ_C incorporates the effect of 'other modes' for normal processes. over the single-mode theory. The effect is to give rise to a 'normal drift' term over and above the Debye term. In a different language we say that the N-drift is the contribution towards the conductivity from the off-diagonal part of the three-phonon N-operator in the phonon Boltzmann equation (see Hamilton 1973; Simons 1975).

We present here the results of our calculations of the N-drift. We use the high temperature approximation $\bar{N} \approx 1/\alpha Gx$ etc. and consider a case where only three-phonon processes are present: $\tau \approx \tau_p$. Then according to Hamilton (1973) we approximate the formula for the N-drift as

$$\begin{aligned} K_{N\text{-drift}} &= \hbar^2/(3N_0 \Omega kT^2) \langle q\omega c\tau/\tau_N \rangle^2 / \langle q^2/\tau_N \rangle (1 - \tau/\tau_N) \\ &\cong \hbar^2/(3N_0 \Omega kT^2) \cdot A/(1+A) \cdot \langle q\omega c \rangle^2 / \langle q^2 \tau_U^{-1} \rangle \\ &= (k/N_0 \Omega) (A/(1+A)) 1/[\sum_s (1/c_s^2) \int dx x^2 \tau_U^{-1}] \end{aligned} \quad (28)$$

$$= A/(1+A) K_{\text{Ziman}}^{\text{smrt}}. \quad (29)$$

Here Ω = volume of a unit cell, $c = c_s$, $\langle f \rangle = \sum_q f_q \bar{N} (\bar{N} + 1)$ with $q \equiv (\vec{q}, s)$

and $A = \langle \tau_N^{-1} \rangle / \langle \tau_U^{-1} \rangle$. Eq. (29) expresses the N-drift result in terms of Ziman's conductivity result in the spirit of the single-mode relaxation time theory (see Parrott 1971).

For Ge we take $\gamma = 2$, $a = 5.65 \text{ \AA}$, $\rho = 5.46 \text{ gm cm}^{-3}$, $\lambda_0 = 0.387.10^{12} \text{ dyn cm}^{-2}$ and $\mu_0 = 0.547.10^{12} \text{ dyn cm}^{-2}$ (λ_0 and μ_0 are Lamé's elastic constants). The results of calculations for the continuum model are tabulated in table 3. In the high temperature region the behaviour $K \propto T^{-1}$ is clearly observed. The results for $K_{\text{Ziman}}^{\text{smrt}}$ are quite convincing. For example, at room temperature (300° K) experimental result for the conductivity of a natural germanium sample is 0.6 (Glassbrenner and Slack 1964), while we obtain 0.68 in the Ziman limit where we consider phonon-phonon interactions alone. At room temperature the resistivity in Glassbrenner and Slack's natural germanium sample due to mass defect scattering comes to about 0.48 (Srivastava, 1975 a). Inclusion of this brings $K_{\text{Ziman}}^{\text{smrt}}$ down to 0.51, which is below the experimental result. (This should be the case in the Ziman limit). N-drift is found to be about 43.2% of the Ziman result in the high temperature range 300–900° K. With decrease of temperature A , a measure of N- and U-scattering rates, will increase, allowing the N-drift to play important role in thermal conduction in insulators.

Table 3. Calculated results for N-drift in Ge. Only three-phonon processes are considered. Results are compared with the Ziman limit conductivity in the 'single mode' relaxation time approximation.

(Unit: Watt. cm⁻¹ deg.⁻¹)

Temperature (°K)	$K_{N\text{-drift}}$	$K_{\text{Ziman}}^{\text{smrt}}$	$\frac{K_{N\text{-drift}}}{K_{\text{Ziman}}^{\text{smrt}}} \cdot 100\%$
900	0.1075	0.2267	
700	0.1382	0.2915	
500	0.1935	0.4081	43.2%
400	0.2419	0.5102	
300	0.3226	0.6802	

6. Conclusion

We have calculated single-mode relaxation times of phonons in different polarization modes undergoing different three-phonon processes. Effect of inclusion of dispersion in the spirit of the Born-von-Kármán model, *viz.*, analogous to that found in a one-dimensional linear chain, over the continuum model is found to reduce the results in general. In particular U-process relaxation rates are very much affected at low temperatures when such a dispersive model is used. What this dispersive model does is to modify the phonon frequencies by a sine law; and in our reformulation of section, we also use the same law in modifying the three-phonon scattering strengths. In fact one must also consider the same effects in modifying phonon density-of-states and the areas over which the results in eq. (8) and eq. (9) are integrated. These considerations may alter our findings both at low and high temperatures. Finally, it must be pointed out here that the results in eq. (3) express the three-phonon scattering strengths $|A_{q q' q''}|^2$ of S1 in a form used by Leibfried and Schlömann, who make use of the approximation of a one-dimensional linear chain with nearest neighbour forces. An attempt to reformulate the results for $|A_{q q' q''}|^2$ so that these become amenable to modifications due to a dispersive model seems quite difficult; and if possible the calculations are cumbersome.

We have compared our findings for the isotropic continuum model with some earlier works, and agreements/disagreements are discussed. Since our findings are based upon a systematic approach, without use of any adjustable parameters whatsoever, one can be more confident of the results and any applications of these. For example, we find that for a pure crystal at high temperatures where $\tau \cong \tau_p$, the N-drift due to Callaway theory comes to about half of the conductivity result in the Ziman limit. We justify this by saying that K_{Ziman}^{smrt} obtained in the present work satisfied the assertion (Srivastava, 1975 *b*) that the Ziman limit is a lower estimate for the conductivity. Having justified this, we have shown subject to the validity of eq. (29), that the result for the normal-drift is convincingly correct.

Finally, we remark on the validity of the single-mode relaxation time assumption. As we have seen, the effect of the off-diagonal part of N-operator is to give rise to an additional positive contribution in addition to the result due to the diagonal part of the phonon collision operator. The effect of introducing the off-diagonal part of the U-operator is a matter of some controversy (*see* Hamilton, 1973; Simons 1975). The author believes that there is a lot more to be said about the introduction of the off-diagonal part of the phonon collision operator; and hopes to present some results in due course.

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