

Comparison of high-temperature three-phonon resistivities from different theoretical models

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Abstract. We present a comparison of high-temperature three-phonon resistivities from the relaxation time methods due to Klemens, Callaway, and Debye, and the variational method due to Leibfried and Schlömann. All the calculations are based upon the same choice of anharmonic crystal potential; and hence the results are suitable for comparison on quantitative basis. We find that the resistivities in increasing order of magnitude come from the methods due to Klemens, Callaway Debye, and Leibfried and Schlömann respectively.

Keywords. Lattice thermal conductivity; phonon relaxation.

1. Introduction

Because of lack of reliable result for three-phonon relaxation times it has not been possible so far to give any quantitative analysis for three-phonon resistivities due to various models and this is due to two main reasons. Firstly, different workers in the field have considered different crystal anharmonic potential. Since three-phonon scattering strengths are decided by anharmonic potential, the magnitude of three-phonon relaxation times obtained by different workers differ from each other. Secondly, different workers have described different ways of dealing with the conditions imposed by energy and momentum conservation. This yields different frequency and temperature dependence for three-phonon relaxation times.

For example, in the pioneer works of Klemens (1951) and Leibfried and Schlömann (1954) the magnitude of the crystal anharmonic potential is not similar. This disagreement has been pointed out at many places (*see e.g.*, Roufosse and Klemens 1973—abbreviated hereafter as RK). What is more important is that neither of these is correct (*see* Hamilton and Parrott 1969; Parrott and Stuckes 1975). Probably the most reliable estimate is due to Hamilton and Parrott (1969). Parrott (1972) has correlated the result of Hamilton and Parrott with a corrected form of Leibfried and Schlömann.

The second factor deserves equally important attention. Let us first consider the umklapp relaxation times. Frequency dependence for the same has been considered as proportional to q^2 by Klemens (1951) and others (*e.g.*, RK), but q in 1958; and recently Mikhail and Simons (1975) have shown it to be propor-

tional to q^3 . So there can be a considerable amount of unreliability in the results of calculations from these different pictures. For normal processes Callaway (1959) took q^2 dependence, while Parrott (1963, 1972) and Jackson and Walker (1971) have suggested q dependence to be more appropriate. Herring (1954) however obtained a general picture q^n , $n = 1, 2, 5/2, 3$ or 4 depending upon the particular combination of phonon polarizations involved in three-phonon processes. Also, different authors have considered different combinations of polarizations to give the most important contribution. For example, Benin (1972) found the process $t + t \rightleftharpoons 1$ to dominate the thermal resistance, while Mikhail and Simons (1975) accept that $t + 1 \rightleftharpoons 1$ is the dominant process. Author's recent calculations (1975), however, support Benin's finding.

Thus it is desirable to follow a systematic approach for calculating normal and umklapp relaxation times, and thence compare the results of resistivity calculations from different models. In the present paper we consider our recent formulation (1974, 1976) of phonon anharmonic relaxation times, and evaluate Klemens, Callaway and Debye terms for the conductivity, and compare them with the Ziman limit (which is the same as the treatment Leibfried and Schlömann's) calculations presented by the author elsewhere (1975). Also we point out that the treatment of the variational Ziman limit result in the spirit of the single-mode relaxation time picture does not give the same result. We evaluate the latter, viz., K'_s , and then compare it with Klemens result. The ratio thus obtained is explained theoretically and the disagreement with the recent finding of RK is discussed.

Separate contributions from longitudinal and transverse phonons towards the Debye term is evaluated and some earlier and contemporary works are criticised.

2. Relaxation time results for the conductivity

A generalized form of the conductivity result due to Debye is

$$K_D = \frac{\hbar^2}{3N_0 \Omega k T^2} \langle \tau \omega^2 c^2 \rangle \quad (1)$$

where $N_0 \Omega$ is volume of the crystal, k is the Boltzmann constant, \hbar is Planck's constant divided by 2π , T is absolute temperature, $c = c_s(\mathbf{q})$ is velocity for phonons with frequency $\omega = \omega_s(\mathbf{q})$, τ is combined single-mode relaxation time $\tau^{-1} = \tau_N^{-1} + \tau_u^{-1}$ (we consider in this paper only three-phonon processes), and $\langle \rangle = \sum_{\mathbf{q}} f_{\mathbf{q}} \bar{N} (\bar{N} + 1)$; $\mathbf{q} = (\mathbf{q}, s)$ and \bar{N} is Planck's distribution function for phonons.

Klemens' conductivity result follows from eq. (1) if we simply ignore the normal (N) processes:

$$K_K = \frac{\hbar^2}{3N_0 \Omega k T^2} \langle \tau_U \omega^2 c^2 \rangle. \quad (2)$$

Callaway took into account the momentum conservation property of normal processes and improved the Debye single-mode relaxation time (abbreviated as smrt) result by adding a term to eq. (1) which is really a contribution from the off-diagonal N collision operator (see Simons 1975):

$$K_C = \frac{\hbar^2}{3N_0\Omega kT^2} \left[\langle \tau \omega^2 c^2 \rangle + \frac{\langle \tau q c \omega / \tau_N \rangle^2}{q^2 \tau_N^{-1} (1 - \tau \tau_N^{-1})} \right]. \quad (3)$$

Going to high temperature approximation $\bar{N} = kT/\hbar\omega$ we can express the above results as follows:

$$K_D = (k/N_0\Omega) \sum_s c_s^2 \int_0^1 dx (x^2/\tau^{-1}) \quad (1')$$

$$K_K = (k/N_0\Omega) \sum_s c_s^2 \int_0^1 dx (x^2/\tau_U^{-1}) \quad (2')$$

and

$$K_C = (k/N_0\Omega) \left[\sum_s c_s^2 \int_0^1 dx (x^2/\tau^{-1}) + \frac{(\sum_s \int_0^1 dx x^2 \tau \tau_N^{-1})^2}{(\sum_s c_s^{-2} \int_0^1 dx x^2 (1 - \tau/\tau_N) \tau_N^{-1})} \right] \quad (3')$$

with $x = |q|/q_D$, and q_D as Debye radius.

Following our previous work (1974) we write the results for τ^{-1} :

$$\begin{aligned} \tau_q^{-1} &= \frac{\hbar q_D^5}{32 \pi \rho} \sum_{\substack{s' s'' \\ \epsilon}} \frac{1}{\alpha \alpha' \alpha''} \int dx' x'^2 \left| \frac{A_{qq'q''}}{\lambda + 2\mu} \right|^2 \\ &\times \left\{ 2(Cx + Dx') \left[(1 - \epsilon + \epsilon(Cx + Dx')) \right] \frac{\bar{N}'(\bar{N}'' + 1)}{(\bar{N} + 1)} \right. \\ &\left. + (Cx - Dx') \left[(1 - \epsilon + \epsilon(Cx - Dx')) \right] \frac{\bar{N}'\bar{N}''}{\bar{N}} \right\}. \quad (4) \end{aligned}$$

Here $\alpha = c_s/c_1$, $\alpha' = c_{s'}/c_1$, $\alpha'' = c_{s''}/c_1$, $C = c_s/c_{s''}$, $D = c_{s'}/c_{s''}$, $c_1 = \sqrt{(\lambda + 2\mu)/\rho}$, λ and μ being Lamé's second-order elastic constants, and $|A_{qq'q''}|^2$ are called three-phonon scattering strengths. The symbol ϵ takes values 1 and -1 for N and U processes respectively. The first and second terms in eq. (4) come from three-phonon events of the types $q + q' \rightleftharpoons (-q'')$ and $(-q) \rightleftharpoons q' + q''$ respectively. Further, we express, following Parrott (1972)

$$\left| \frac{A_{qq'q''}}{\lambda + 2\mu} \right|^2 = \left| \frac{A_L}{\lambda + 2\mu} \right|^2 \alpha^2 \alpha'^2 \alpha''^2 \quad (5)$$

for an isotropic continuum model, with

$$A_L = \sqrt{10/3} \frac{2\rho (\gamma + \frac{1}{2}) c_1^3}{a\omega_D}, \quad (6)$$

where ρ is mass density, a is the cubic lattice constant, ω_D is the Debye frequency and γ is the Grüneisen constant for the material. With eqs (5) and (6) the result in the high temperature approximation for τ^{-1} becomes

$$\tau_a^{-1} = \frac{kT q_D^4 a^3}{32\pi\rho c_1} \left| \frac{A_L}{\lambda + 2\mu} \right| \sum_{\substack{\epsilon \\ s', s''}} 1/a'' \int dx' x x' \\ \times \{2 [1 - \epsilon + \epsilon(Cx + Dx')] + (1 - \epsilon + \epsilon(Cx - Dx'))\}. \quad (7)$$

It can be noticed, however, that the above result for the relaxation times corresponds to our earlier set of results (1976).

For the isotropic continuum model the energy conservation condition, viz., $\omega \pm \omega' = \omega''$ and the momentum conservation condition, viz., $\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = \mathbf{G}$, \mathbf{G} being a reciprocal lattice vector, allow the following processes:

$(-q) \rightleftharpoons q' + q''$:

$$1 \rightleftharpoons 1 + 1; \quad t \rightleftharpoons t + t \quad (N \text{ only})$$

$$1 \rightleftharpoons 1 + t; \quad 1 \rightleftharpoons t + t \quad (N \text{ and } U \text{ both})$$

$q + q' \rightleftharpoons (-q'')$:

$$1 + 1 \rightleftharpoons 1; \quad t + t \rightleftharpoons t \quad (N \text{ only})$$

$$1 + t \rightleftharpoons 1;$$

$$t + 1 \rightleftharpoons 1; \quad t + t \rightleftharpoons 1. \quad (N \text{ and } U \text{ both}).$$

It should be noticed here that processes $t + t \rightleftharpoons t$; $t \rightleftharpoons t + t$; and $1 + 1 \rightleftharpoons 1$; $1 \rightleftharpoons 1 + 1$ are allowed only in the isotropic continuum model where broadening effect, as suggested by Bross (1962) and Simons (1963), may favour them. However, Hamilton and Parrott suggest that scattering strength for $t + t \rightleftharpoons t$ (and hence $t \rightleftharpoons t + t$) is zero. Therefore we simply ignore them. The limits of integrations over the variable x' for these processes are presented in author's previous papers (1974, 1975, 1976).

From eqs (1') and (2') it is clear that we can separate contributions from separate polarizations towards K_D and K_K . However, the normal-drift term in eq. (3') does not permit us to express K_C as being contributed by separate polarizations explicitly.

3. Comparison of relaxation time results with the variational Ziman limit result

The variational result for the conductivity due to Leibfried and Schlömann is in fact the Ziman limit. The high temperature expression for the same is presented in our previous paper (1975). It is

$$K_C = \frac{\rho c_1^3}{3\pi q_D T} \left| \frac{\lambda + 2\mu^2}{A_L} \right| \frac{1}{\iint dx dx' x x' \{ [2 - r(x + x')] + (2 - rx - x') \}} \quad (8)$$

where $r = c_1/c_2$. This takes into account the full phonon collision operator and hence is expressed in such a way that only processes of the type $q + q' \rightleftharpoons (-q'')$ (U only) contribute. Further, symmetry and indistinguishability considerations allow only the processes $t + 1 \rightleftharpoons 1$ (U) and $t + t \rightleftharpoons 1$ (U) to describe the situation.

If we express the Ziman limit in the spirit of the smrt picture, then it can be written at high temperatures as (see e.g., RK)

$$K_Z' = k/(N_0\Omega) \frac{1}{\sum_x 1/(c_s^2) \int_0^1 dx x^2 \tau_U^{-1}} \quad (9)$$

With this, we rewrite, with the help of eqs (1'-3'),

$$K_K = (1 + A) K_D \quad (10)$$

$$K_C = K_D + A/(1 + A) K_Z' \quad (11)$$

$$= 1/(1 + A) [K_K + AK_Z'] \quad (12)$$

where $A = \{\tau_N^{-1}\}_{av}/\{\tau_U^{-1}\}_{av}$, which can at least be used at high temperatures. Expressing K_C in terms of A is not necessary at all, but helps in understanding the same in terms of relative strengths of N and U processes. Defining K_K as in eq. (10) not only helps in its interpretation at high temperatures, but also is useful in performing calculations as we shall see in the next section. K_K comes from the smrt result, viz., K_D under the condition when the role of N processes can be neglected in comparison to U processes. K_C makes a balance between the two extreme situations, viz., N processes very weak (K_K) and N processes infinitely strong (K_Z').

4. Results and discussion

We evaluate K_D , K_C , $K_0^<$, K_Z' , numerically, using eqs (1'), (3'), (8) and (9) respectively, with eq. (7). K_K is evaluated, however, using eq. (10). The reason why we use eq. (10) instead of eq. (2') is that numerical evaluation of K_K from eq. (2') gives computing interruption. This is obvious, because for $x < x_0$ (the reduced wave vector at which an U process starts) the integrand in eq. (2') becomes infinite. Use of eq. (10) saves us from that difficulty and at the same time does not lead to any inaccuracy for the high temperature results. The parameters used in the calculations for Ge are taken from our previous papers. The results of calculations are presented in tables 1 and 2.

We note that the calculated results are in the order $W_K < W_C < W_D < W_0^>$. This means when N processes are neglected one gets a lower estimate (W_K) for the smrt resistivity (W_D). In the Callaway approach the N-drift term is an improvement over the result K_D ; and hence $W_C < W_D$. The Ziman limit result from the Leibfried and Schlömann approach, which considers N processes infinitely strong, brings the highest measure of resistivity.

Our calculations give $W_0^> = 2.85 W_K$, and $W_0^> = 1.59 W_Z'$, so that $iW_Z'/W_K = 1.79$ at high temperatures. Let us obtain this ratio theoretically. We can write, at high temperatures,

Table 1. Comparison of conductivity results (only three-phonon processes a considered)
unit: Watt cm⁻¹ K⁻

$K_0^<$	K_z^r	K_D	K_C	K_K
0.142	0.226	0.211	0.318	0.405

Table 2. Contribution from separate polarization modes towards the conductivity in the smrt picture, and the parameter A

$K_D(1)$	$K_D(t)$	K_D	A
0.059	0.152	0.211	.91

$$\frac{W_Z^r}{W_K} = \frac{(\sum_s 1/c_s^2 \int_0^1 dx x^2 \tau_U^{-1}) (\sum_s c_s^2 \int_0^1 dx x^2 \tau_U)}{(\sum_s \int_0^1 dx x^2)^2}$$

$$= \left(\sum_s 1/c_s^2 \int_0^1 dx x^2 \tau_U^{-1} \right) \left(\sum_s c_s^2 \int_0^1 dx x^2 \tau_U \right)$$

From here it follows that

$$W_Z^r/W_K = 1.8 \quad \text{when} \quad \tau_U^{-1} \propto \omega^2. \tag{13}$$

Therefore, theoretically, we see that in the smrt picture the ratio of lattice thermal resistances in the limit of N processes infinitely strong to N processes negligibly small comes out to be 1.8. Our calculated results give almost the same ratio and hence can be regarded as very convincingly correct.

However, RK have shown that their approach gives for W_K a result W_{RK} which is 6.8 times W_{LS} (a result obtained by Leibfried and Schlömann for $W_0^>$). We attribute two factors in explaining the wrong finding of RK in comparison to our convincingly correct result, viz., $W_0^> = 2.85 W_K$. As we pointed out in our previous paper (1976), these authors consider a result for τ_q^{-1} which is 16 times greater than what is normally expected. Consideration of this will make RK's ratio as $W_{LS}/W_{RK} = 2.35$. Also, let us compare RK's summation procedure with ours (GP):

$$\left(\sum_{q'} \right)_{RK} \rightarrow \frac{N_0 \Omega (\mathbf{q} + \mathbf{G})^2}{8 \sqrt{2} \pi^2} \int d|\mathbf{q}'|$$

$$\rightarrow \frac{N_0 \Omega q_D G^2}{8 \sqrt{2} \pi^2} \int dx' \tag{14}$$

$$\left(\sum_{q'} \right)_{GP} \rightarrow \frac{N_0 \Omega q_D^3}{8 \pi^3} 2\pi c'' \int dx' x'^2 \int d\theta' \sin \theta' \delta(\Delta \omega)$$

(where $\cos \theta' = \hat{q} \cdot \hat{q}'$)

$$\rightarrow \frac{N_0 \Omega q_D^3}{4 \pi^2} \int dx' \tag{15}$$

so that

$$\begin{aligned} \frac{(\sum_{\mathbf{q}})_{RK}}{(\sum_{\mathbf{q}'})_{GP}} &= \frac{G^2}{2\sqrt{2}q_D^2} \\ &= \sqrt{2} \quad \text{for } |\mathbf{G}| = 2q_D. \end{aligned} \quad (16)$$

Therefore, assuming that our summation procedure is fairly reasonable for the isotropic continuum model of the crystal, we note that RK's summation procedure should be divided by a factor of $\sqrt{2}$ in order to yield correct result. Employing this correction their ratio should finally become

$$W_{LS}/W_{RK} = 2 \cdot 35 \cdot (\sqrt{2}) = 3 \cdot 31. \quad (17)$$

This ratio, *viz.*, 3.31, differs from our result, *viz.*, 2.85, by a factor of 1.16. We again attribute this discrepancy to three factors. First, RK consider that the summation over the polarization indices s' and s'' introduces a factor of 4: $\sum_{s's''} \rightarrow 4$ [their assumption (ii) on page 5832 of their paper]. Let us see whether or not it is the case. We write, symbolically,

$$\begin{aligned} K_K &\rightarrow \sum_s 1/\tau_U^{-1} \\ &\rightarrow \sum_s \frac{1}{\sum_{s's''} [\tau_U^{-1}(s + s' \rightleftharpoons s'') + \tau_U^{-1}(s \rightleftharpoons s' + s'')]} \end{aligned}$$

Now we can sum over s' and s'' to write the denominator as (*see* Srivastava 1974)

$$\begin{aligned} &\sum_{s's''} [\tau_U^{-1}(s + s' \rightleftharpoons s'') + \tau_U^{-1}(s \rightleftharpoons s' + s'')] \\ &= \tau_U^{-1}(t + 1 \rightleftharpoons 1) + 2[\tau_U^{-1}(1 + t \rightleftharpoons 1) + \tau_U^{-1}(t + t \rightleftharpoons 1)] \\ &\quad + 4[\tau_U^{-1}(1 \rightleftharpoons 1 + t) + \tau_U^{-1}(1 \rightleftharpoons t + t)]. \end{aligned}$$

This suggests that a factor of 4 comes only for type II processes ($s \rightleftharpoons s' + s''$), and not for type I processes. Therefore we suggest that RK have over-counted the occurrence of type I processes. Secondly, RK neglect the cross term while averaging over the angles between \mathbf{q} and \mathbf{G} : they write

$$(\mathbf{q} + \mathbf{G})^2 = q^2 + G^2 \quad (18)$$

$$\simeq G^2, \quad (19)$$

i.e., they further neglect q^2 relative to G^2 . But since \mathbf{q} should make an acute angle with \mathbf{G} (*see* Simons 1975) for a U process to take place, we can write

$$\begin{aligned} (\mathbf{q} + \mathbf{G})^2 &= q^2 + G^2 + 2|\mathbf{q}||\mathbf{G}|\cos\eta \\ &= q_D^2(x^2 + 4 + 4x|\cos\eta|). \end{aligned}$$

Taking $|\cos\eta| = 1/\sqrt{3}$, as the RMS value for an angle between two random

directions. We can approximate the above to $5.4 q_D^2$ for $x = 1/2$, and $7.3 q_D^2$ for $x = 1$. These values are less than $G^2 = 4 q_L^2$ by factors of 1.35 and 1.83 respectively. This illustration shows that neglect of the cross term by RK is also responsible for their wrong finding. Thirdly, Leibfried and Schlömann use some averaging procedure in obtaining their result W_{LS} . In particular, we like to mention that they approximate their integral at high temperatures by $\sum_G J_{i's'}$ (G) = 1, without evaluating the same over suitable integration domains. Proper evaluation of J may modify the numerical factor in W_{LS} .

Table 2 shows that at 900 K longitudinal phonons contribute about 28% of the total heat predicted by the Debye term K_D . This finding suggests that in the smrt treatment longitudinal phonons play quite important part in heat conduction at high temperatures. This is in disagreement with a qualitative picture by Sharma *et al* (1971) and Dubey (1976 *a*) who assume that at high temperatures almost all heat is transported by transverse phonons. Also, in the high temperature approximation the parameter A is obtained to be 0.91 at 900 K. This suggests that at high temperatures N processes are almost as strong as U processes. With this value of A we obtain the normal-drift to be half in magnitude of K_D . This overrules the suggestion by Sharma *et al* (1971) and Dubey (1976 *b*) that normal-drift is negligible in Ge. Table 2 gives contributions from separate polarization modes, and the parameter A .

The conclusions drawn in this paper, although exhibited for Ge alone, should come true at least for crystals showing cubic symmetry, where use of an isotropic model can be made without introducing appreciable error. However, use of the continuum model at high temperatures should no longer be regarded as fair. A suitable dispersion law must be used. But a proper use of a dispersive model will not be so easy, and as far as qualitative picture for the present intercomparison of results is concerned not much difference should be expected. The work was completed at UWIST, Condiff.

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