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Thermal resistivity of dielectric crystals due to four-phonon processes and optical modes*

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The interaction rate of four-phonon processes at high temperatures is derived in terms of the Grüneisen constant and its dilational derivative. The interaction arises in part from quartic anharmonicities and in part from cubic anharmonicities to second order. The four-phonon relaxation rate varies as the square of the frequency and the square of the temperature. It is compared to the three-phonon relaxation rate and found to be weaker by at least a factor 30 at 1000 K. The anharmonic interaction between two acoustic phonons and one optical phonon does not only limit the lifetime of optical phonons, but also contributes to the relaxation rate of acoustic modes in thermal conduction. It is shown that this relaxation rate is similar in magnitude and temperature dependence to the relaxation rate due to processes involving three acoustic phonons. The frequency dependence is also similar except at low frequencies, since the interaction is forbidden at lowest frequencies. Neither of the interactions considered here can quantitatively explain the observation that the thermal resistance of many dielectric crystals at high temperatures varies more rapidly than linearly with temperature.

I. INTRODUCTION

The theories of Debye[1] and Peierls[2] predict the phonon mean free path limited by cubic anharmonicities to vary inversely as the absolute temperature T at sufficiently high temperatures, so that the thermal conductivity K should also vary as $1/T$. This is approximately true, but it is often observed that K varies more rapidly than $1/T$ at high temperature, so that the thermal resistivity $W = 1/K$ may be expressed as

$$W = aT + bT^2 , \tag{1}$$

where the quadratic term is appreciable.[3] The linear term is ascribed to three-phonon processes, and it seems natural to ascribe the quadratic term to four-phonon processes.[3] Four-phonon processes were first discussed by Pomeranchuk,[4] who invoked them not as a direct source of thermal resistance, but to eliminate a divergence in the thermal-conductivity integral due to low-frequency longitudinal waves. He predicts K to vary more rapidly than $1/T$, though not of the same form as Eq. (1). Equation (1) implies that four-phonon processes are strong enough to appreciably affect the mean free path of all phonons.

We shall estimate the strength of four-phonon processes by comparing them to the strength of the three-phonon processes. It will be seen that four-phonon processes are much weaker than three-phonon processes. Thus if one disregards the special role of longitudinal low-frequency phonons and assumes that the thermal conductivity is governed by the mean free path of the high-frequency modes, one must conclude that the term bT^2 in (1) should be much smaller than observed, i.e., less than 3% of the total around 1000 K, instead of about 20% as typically observed.[3]

Another interaction which might lead to a variation of W with T more rapid than linear is the interaction of two acoustic modes with an optical mode. This process, which has been considered qualitatively,[5] will be estimated quantitatively, relating the mean free path of the acoustic mode to the lifetime of the optical mode.[6] It will be seen that this process does not lead to a term in the thermal resistivity which would explain the observed rapid variation of W with T at high temperatures.

The observed rapid variation of the thermal resistivity with temperature can thus not be ascribed to either interaction. It has been shown that it is due in part to thermal expansion, and in the case of single crystals to the special role of low-frequency longitudinal phonons.[7] The role of thermal expansion was first considered by Ranninger.[8]

II. ANHARMONIC PERTURBATIONS

Progressive lattice waves form the normal modes of a regular crystal only if the lattice forces are completely harmonic, i.e., if the potential energy is quadratic in the displacements or strains.[9] The displacement of an atom at site $\vec{x}$ due to a lattice wave of wave vector $\vec{q}$ may be written

$$\vec{u}(\vec{x}) = (1/\sqrt{G})\vec{\epsilon}a(\vec{q})e^{i\vec{q}\cdot\vec{x}} , \tag{2}$$

where $\vec{\epsilon}$ is a unit vector in the direction of polarization, G is the number of unit cells in the crystal, and $a(\vec{q})$ a time-dependent displacement amplitude, containing the factor $e^{i\omega t}$. The unperturbed Hamiltonian for each normal mode is

$$H^0(\vec{q}) = \tfrac{1}{2}M\omega^2[a^*(\vec{q})a(\vec{q}) + a(\vec{q})a^*(\vec{q})] . \tag{3}$$

The lattice waves are quantized: a and a^* are annihilation and creation operators of the equivalent harmonic oscillators. Their nonvanishing matrix elements are

$$\begin{aligned} [a(\vec{q})]_{N,N-1} &= (\hbar/M\omega)^{1/2}N^{1/2}\,, \\ [a^*(\vec{q})]_{N,N+1} &= (\hbar/M\omega)^{1/2}(N+1)^{1/2}\,, \end{aligned} \tag{4}$$

where N is the number of phonons in the mode.

The anharmonic terms in the potential energy give rise to higher-order terms in the Hamiltonian. Terms which are cubic and quartic in the displacements are of the form

$$H_{(3)} = \sum_{\vec{q},\vec{q}\,',\vec{q}\,''} c_3(\vec{q},\vec{q}\,',\vec{q}\,'')a(\vec{q})a(\vec{q}\,')a^*(\vec{q}\,'') \tag{5}$$

and

$$H_{(4)} = \sum_{\vec{q},\vec{q}\,',\vec{q}\,'',\vec{q}\,'''} c_4(\vec{q},\vec{q}\,',\vec{q}\,'',\vec{q}\,''') \times a(\vec{q})\,a(\vec{q}\,')a^*(\vec{q}\,'')a^*(\vec{q}\,''')\,. \tag{6}$$

These give rise, in first-order perturbation, to three-phonon and four-phonon processes, respectively.

Because the anharmonic lattice forces reside in linkages which are uniformly distributed throughout the crystal except for the modulation of the basic crystal structure, the coefficients c_3 and c_4 vanish unless they satisfy the interference conditions

$$\vec{q}+\vec{q}\,'-\vec{q}\,''-\vec{q}\,'''=\vec{b}\,, \tag{7}$$

where $\vec{b}$ is zero or an inverse lattice vector. Real processes must also satisfy frequency or energy conservation, i.e.,

$$\Delta\omega \equiv \omega+\omega'-\omega''-\omega'''=0\,. \tag{8}$$

For three-phonon processes, $\vec{q}\,'''$ and ω''' are omitted in (7) and (8). The terms in (5) and (6) describe processes where phonons $\vec{q}$ and $\vec{q}\,'$ are on the same side of the balance equation. By inverting the role of a and a^* and changing the sign of the wave vector and frequency in (7) and (8), other processes can be described similarly.[9]

The rate of change of the phonon occupation number N of mode $\vec{q}$ due to three-phonon and four-phonon processes can be obtained in terms of the coefficients c_3 and c_4 and becomes

$$\left(t\frac{dN}{dt}\right)_{(3)} = 2\left(\frac{\hbar}{M}\right)^3 \sum_{\vec{q}\,',\vec{b}} |c_3|^2 \frac{1}{\omega\omega'\omega''}\,\frac{1-\cos\Delta\omega t}{\Delta\omega^2} \times[(N+1)(N'+1)N''-NN'(N''+1)]\,, \tag{9}$$

$$\left(t\frac{dN}{dt}\right)_{(4)} = 2(\hbar/M)^4 \sum_{\vec{q}\,',\vec{q}\,'',\vec{b}} |c_4|^2(\omega\omega'\omega''\omega''')^{-1} \times\frac{1-\cos\Delta\omega t}{\Delta\omega^2}[(N+1)(N'+1)N''N''' - NN'(N''+1)(N'''+1)]\,. \tag{10}$$

The resonance factor ensures that the principal contributions in the summation arise from processes for which $\Delta\omega=0$, and that the change in N is linear in t. In (9), $\vec{q}\,''$ is given by (7), though its polarization is not determined; similarly $\vec{q}\,'''$ is determined in (10). In (9), the restriction $\Delta\omega=0$, together with (7), restrict $\vec{q}\,'$ to lie on a surface in wave-vector space for each value of $\vec{b}$, and on another surface if the role of $\vec{q}\,'$ in the balance equation is reversed. In (10), $\vec{q}\,''$ can take any value. For each value of $\vec{q}\,''$, $\vec{q}\,'$ will again lie on a surface in $\vec{q}$ space; there will be one such surface for each $\vec{b}$ and for each sign of $\vec{q}\,'$ and $\vec{q}\,''$ in the balance equation.

To find the interaction rates, one must know the coefficients c_3 and c_4, and one has to perform the summations over the interacting phonons, subject to the restrictions (7) and (8).

The coefficients c_3 and c_4 are related to the anharmonic terms of the potential energy of the linkages between atoms. The linkages have positions in the lattice, and c_3 can be expressed in terms of the $\vec{b}$th Fourier coefficient of the cubic terms of the potential energy, as first outlined by Peierls.[2] Similarly one can relate c_4 to the $\vec{b}$th Fourier coefficient of the quartic terms of the potential energy of the linkages. However, we usually lack the detailed information about the interatomic forces which would be required for that procedure. Since the anharmonicities also manifest themselves in the equation of state, in particular the thermal expansion, it is advantageous to express c_3 and c_4 in terms of Grüneisen coefficients.

In the Grüneisen approximation, the frequency of a lattice mode of wave vector $\vec{q}$ is changed from $\omega_0(\vec{q})$ to $\omega(\vec{q})$ if the crystal undergoes a dilatation Δ, so that

$$\omega(\vec{q}) = \omega_0(\vec{q})[1-\gamma(\vec{q})\Delta-\tfrac{1}{2}\gamma'(\vec{q})\Delta^2-\cdots]\,, \tag{11}$$

where $\gamma(\vec{q})$ and $\gamma'(\vec{q})$ are the first and second Grüneisen coefficients,[10] generally functions of mode $\vec{q}$, and γ' is the derivative γ with respect to Δ. The coefficients $\gamma(\vec{q})$ enter into the expression for thermal expansion.

One can write (3) in the form

$$H^0(\vec{q}) = \frac{1}{G}\sum_{\vec{x},\vec{q}\,'} M\omega\omega' a^*(\vec{q}\,')a(\vec{q})(\vec{\epsilon}\cdot\vec{\epsilon}\,')\exp[i(\vec{q}-\vec{q}\,')\cdot\vec{x}]\,, \tag{12}$$

where the summation over $\vec{q}\,'$ also includes the three polarizations. A change in H^0 due to a dilatation Δ arises from the change in the factor $\omega\omega'$. Now

$$\omega\omega' = \omega_0\omega_0'\{1-[\gamma(\vec{q})+\gamma(\vec{q}\,')]\Delta + [\gamma(\vec{q})\gamma(\vec{q}\,')-\tfrac{1}{2}\gamma'(\vec{q})-\tfrac{1}{2}\gamma'(\vec{q}\,')]\Delta^2-\cdots\}\,,$$

$$\omega\omega' = \omega_0\omega_0'[1-2\gamma\Delta+(\gamma^2-\gamma')\Delta^2-\cdots]\,, \tag{13}$$

where it is assumed, for simplicity, that γ and γ'

are the same for all modes.

While the summation in (12) rejects all terms except those for which $\vec{q}' = \vec{q}$ and $\vec{\epsilon}' = \vec{\epsilon}$, this is no longer the case when Δ is not uniform but a function of position. Substituting for Δ the strain of a third lattice wave $\vec{q}''$, and for Δ^2 the strains of a pair of lattice waves $\vec{q}''$ and $\vec{q}'''$, we obtain nondiagonal terms in the perturbation Hamiltonian, which can be identified with the perturbation terms of expressions (5) and (6).

One thus obtains, as shown in Ref. 9,

$$c_3 = 2M(3G)^{-1/2}(\gamma/v)\omega\omega'\omega'' , \tag{14}$$

since

$$\Delta(\vec{x}) = (G)^{-1/2} \sum_{\vec{q}''} (\vec{\epsilon}''\cdot\vec{q}'')e^{i\vec{q}''\cdot\vec{x}}a(\vec{q}'') , \tag{15}$$

and since one may replace $(\vec{\epsilon}''\cdot\vec{q}'')$ by $\omega''/(v\sqrt{3})$, $1/\sqrt{3}$ being the root-mean-square value of the cosine of a random angle. Similarly, since

$$\Delta^2(\vec{x}) = (G)^{-1} \sum_{\vec{q}'',\vec{q}'''} (\vec{\epsilon}''\cdot\vec{q}'')(\vec{\epsilon}'''\cdot\vec{q}''')a^*(\vec{q}''')a(\vec{q}'') \times \exp[i\vec{x}\cdot(\vec{q}''-\vec{q}''')] , \tag{16}$$

one obtains

$$c_4 = M(3G)^{-1}v^{-2}(\gamma^2-\gamma')\omega\omega'\omega''\omega''' . \tag{17}$$

Both (14) and (17) are only rough approximations, which indicate the order of magnitude of the interaction matrix elements and their dependence on other parameters, rather than reliable numerical values. More significantly, however they relate the magnitudes of c_3 and c_4, since similar approximations were made to obtain them.

III. FOUR-PHONON PROCESSES

The rate of change of the phonon occupation number of a given mode $\vec{q}$ can be obtained from (9) and (10). The major problem is the sum over the participating modes. This requires knowledge of the locus of $\vec{q}'$ in (9), and the locus of $\vec{q}'$ for each value of $\vec{q}''$ in (10). Rather than finding each interaction rate separately, we shall aim to find the relation between them.

For simplicity we shall confine ourselves to the high-temperature limit, when $N' = kT/\hbar\omega$, etc., where k is the Boltzmann constant. We assume that modes $\vec{q}'$, $\vec{q}''$, and $\vec{q}'''$ are in thermal equilibrium; only the mode $\vec{q}$ departs from its equilibrium occupation by an amount n. The relaxation rate of mode $\vec{q}$ is defined as

$$1/\tau = -(1/n)dN/dt . \tag{18}$$

In (9), the factor in square brackets—the occupation number factor—becomes

$$[(N+1)(N'+1)N'' - N(N''+1)N'] = -n(N'-N'') = -n(kT/\hbar)\omega/\omega'\omega'' , \tag{19}$$

since $\omega = \omega'' - \omega'$. Similarly one obtains for the occupation number factor in (10),

$$[(N+1)(N'+1)N''N''' - NN'(N''+1)(N'''+1)] = -n[N'(N''+N''') - N''N'''] = -n(kT/\hbar)^2\omega/\omega'\omega''\omega''' . \tag{20}$$

For three-phonon processes one substitutes (14) and (19) into (9), and expresses the sum over $\vec{q}'$ as an integration over $\Delta\omega$, and an integration over the surface $\Delta\omega = 0$ in $\vec{q}'$ space. Approximating that surface by a sphere, of radius $\frac{1}{2}|\vec{q}+\vec{b}| \simeq \frac{1}{2}b$, as done by Roufosse and Klemens,[11] one obtains for a simple lattice

$$1/\tau_{(3)} = 4\pi\frac{a}{v}\gamma^2(kT/Mv^2)\omega^2 , \tag{21}$$

where a^3 is the atomic volume.

One proceeds similarly to get the four-phonon relaxation rate by substituting (17) and (20) into (10), so that

$$\frac{1}{\tau_{(4)}} = 2\pi M^2 \sum_{\vec{b}} \frac{a^6}{(2\pi)^6} \int d^3q'' \int \frac{1}{v}\, d^2q' \,\frac{\omega\omega'\omega''\omega'''}{9v^4} \times (\gamma^2-\gamma')^2\frac{\hbar^2}{M^4}\left(\frac{kT}{\hbar}\right)^2 \frac{\omega}{\omega'\omega''\omega'''} . \tag{22}$$

The integration over $\vec{q}''$ is over the entire zone, while the integration over $\vec{q}'$ is over the surface determined by $\Delta\omega = 0$. This surface depends on $\vec{q}''$. For every value of $\vec{q}''$ there is a set of solutions or surface which can be brought into one-to-one correspondence with the solutions for $\vec{q}'$ in the three-phonon interaction for a given phonon $\vec{q}$, except that now the phonon $(\vec{q}, \omega)$ is replaced by a hypothetical phonon of wave vector $\vec{q}-\vec{q}''$ and frequency $\omega - \omega''$. Analogously to the approximation of Ref. (11) we replace the locus of $\vec{q}'$ by a sphere of radius $\frac{1}{2}|\vec{b}+\vec{q}-\vec{q}''| \simeq \frac{1}{2}b$. We thus obtain from (22),

$$\frac{1}{\tau_{(4)}} = (\gamma^2-\gamma')^2\frac{\pi^2}{18}\frac{k^2T^2}{M^2v^4}\frac{a}{v}\omega^2 . \tag{23}$$

Before accepting Eq. (23), one must also consider four-phonon processes which arise by three-phonon processes to second order. For every group of four phonons which satisfy Eqs. (7) and (8), there are several cases of pairs of successive three-phonon processes of the type

$$\vec{q}+\vec{q}' \to \vec{q}_i \to \vec{q}''+\vec{q}'''+\vec{b} , \tag{24}$$

where $\vec{q}_i = \vec{q}+\vec{q}'$. Other such processes are obtained by permuting $\vec{q}'$, $\vec{q}''$, $\vec{q}'''$, and $\vec{b}$ in (24), each yielding a different intermediate state phonon $\vec{q}_i$. The intermediate state has an energy deficit $-\hbar\Delta\omega_i$, where

$$\Delta\omega_i = \omega_i - \omega - \omega' . \tag{24'}$$

For each $\vec{q}_i$ there are two intermediate states of opposite values of $\Delta\omega_i$. In one case the reaction proceeds as in (24), in the other the second stage preceeds the first and a phonon $\vec{q}_i$ is first "borrowed" and then "restored." The effective perturbation matrix to second order is the product of the two first-order elements divided by $\hbar\Delta\omega_i$, summed over all intermediate states.[12] The effective matrix element for four-phonon processes (24) is thus given by

$$c_4' = \sum_i c_3(\vec{q}, \vec{q}\,', \vec{q}_i) \frac{\hbar}{M\omega_i} \frac{c_3(\vec{q}_i, \vec{q}\,'', \vec{q}\,''')}{\hbar\Delta\omega_i}. \tag{25}$$

It is independent of the occupation number of mode $\vec{q}_i$: N_i cancels when one sums over the two intermediate states for each $\vec{q}_i$. The summation over (25) is for the various $\vec{q}_i$ obtained by permuting the other modes and $\vec{b}$ in (24). Comparing with (17),

$$c_4' = -c_4 \sum_i \frac{\omega_i}{\Delta\omega_i} \frac{2\gamma^2}{\gamma^2 - \gamma'}. \tag{26}$$

In each four-phonon group there is usually only one major contributor to c_4', namely the one for which $\Delta\omega_i$ is least. Also, for each such group the values of $\Delta\omega_i$ can be either positive or negative. Thus, for the total interaction rate, which is proportional to $|c_4 + c_4'|^2$, interference terms between c_4 and c_4' will tend to average out, and $|c_4|^2$ of equation (17) should be replaced by

$$|c_4 + c_4'|^2 = |c_4|^2 \left(\frac{\omega_i}{\Delta\omega_i}\right)^2 \frac{5\gamma^4 + (\gamma')^2 - 2\gamma^2\gamma'}{(\gamma^2 - \gamma')^2}, \tag{27}$$

where $\Delta\omega_i$ is the lowest value of the various intermediate states. When $\Delta\omega_i = 0$, the theory breaks down, because the four-phonon process is really a sequence of two real three-phonon processes. These cases must be excluded from the summation.[12] However, in the vast majority of cases, $\Delta\omega_i$ is comparable to the frequency of the lowest participating mode, so that $(\omega_i/\Delta\omega_i) \simeq 1$. One thus replaces the factor $(\gamma^2 - \gamma')^2$ in (23) by $5\gamma^4 + (\gamma')^2 - 2\gamma^2\gamma'$, so that

$$\frac{1}{\tau_{(4)}} = [5\gamma^4 + (\gamma')^2 - 2\gamma^2\gamma'] \frac{\pi}{18} \frac{k^2 T^2}{M^2 v^4} \frac{a}{v} \omega^2. \tag{28}$$

There are, of course, notable exceptions. When one or two of the participating modes is much smaller than the other modes, $\Delta\omega_i$ is comparable to the lowest frequency while ω_i is approximately equal to the highest frequency. In particular, if ω is much less than $\omega' \sim \omega'' \sim \omega'''$, the factor $\omega_i/\Delta\omega_i$ in (26) becomes of order ω'/ω. Since for the important interactions $h\omega' \sim kT$, (28) must then be enhanced by a factor of order $(kT/h\omega)^2$. This is the case of longitudinal low-frequency phonons discussed by Pomeranchuk,[4] and these processes remove the divergence in the thermal conductivity due to those phonons. In this case, but in this case alone, are the three-phonon processes to second order more important, by an order of magnitude, than the first-order quartic anharmonic processes. The contributions due to longitudinal phonons are thus smaller than calculated in Pomeranchuk's first paper, and make a contribution to the thermal conductivity proportional to $T^{-5/4}$.

However, the relaxation rate of thermal frequency phonons due to four-phonon processes of both types may be estimated by (28), and the term bT^2 in Eq. (1) may be compared to the term aT by comparing (28) to (21). The ratio of the two relaxation rates is

$$\frac{1}{\tau_{(4)}} : \frac{1}{\tau_{(3)}} = \frac{\pi}{72}\left[5\gamma^2 + \left(\frac{\gamma'}{\gamma}\right)^2 - 2\gamma'\right]\frac{T}{T_0}, \tag{29}$$

where $T_0 = Mv^2/k$ is a characteristic temperature of the material. Note that T/T_0 is twice the mean-square thermal strain of an atomic volume element a^3. Typical values of T_0 of hard solids range from 30 000 to 100 000 K.

One concludes that four-phonon processes must be much weaker than three-phonon processes at all temperatures, even in solids with high melting temperatures. Typical values of $\pi/(72T_0)$ would be 10^{-6} K. Thomsen[11] has discussed the pressure dependence of the Grüneisen constant γ; he finds γ' is positive, i.e., of the same sign as γ, and typically comparable to it. In a typical case when $\gamma = \gamma' = 2$, $5\gamma^2 + (\gamma'/\gamma)^2 - 2\gamma' \simeq 5\gamma^2 \simeq 20$. Thus, even if T_0 is as low as 30 000 K, the ratio of the four-phonon to the three-phonon relaxation rates is only 3×10^{-2} at 1000 K. In most cases, however, T_0 is larger and one would expect the ratio to be even smaller.

IV. INTERACTION WITH OPTICAL MODES

Four-phonon processes would yield a component bT^2 in the thermal resistivity (1), but we have seen that this component is too small, by roughly a factor 10, to account for the observations.[3] Another process which would lead to a variation of W with T more rapid than linear, at least over some range of temperatures, is the cubic anharmonic interaction involving two acoustic modes and an optical mode. It is thus of interest to estimate its strength and temperature dependence.

One can apply Eq. (9) to the case when one of the participating modes is an optical mode, except that c_3 is no longer given by (14), since it has been assumed in its derivation that one of the participating modes is of low frequency, so that its effect on the Hamiltonian can be compared to the effect of a uniform strain. Instead, one considers the effect of an internal deformation of each unit cell on the acoustic mode frequencies, matching this internal deformation to the displacement field of the optical mode, as was done in Ref. (6) to obtain

$$c_3 = 2M(3G)^{-1/2}\frac{\gamma}{v}\omega\omega'\omega''\left(\frac{2}{\sqrt{3}}\,\frac{\alpha-\beta}{\alpha+\beta}\right)^{1/2}, \tag{30}$$

where α and β are two effective force constants, such that at the zone boundary

$$\omega_{\text{ac}}^2/\omega_{\text{opt}}^2 = \beta/\alpha\,. \tag{31}$$

If the mode (q, ω) is the optical mode and q', q'' are acoustic modes, then one obtains from (9) and (30) the following expression for the relaxation rate of the optical mode $\vec{q}=0$, summing over all $\vec{q}'$ such that $\vec{q}'' = -\vec{q}'$ and $\omega' = \omega'' = \frac{1}{2}\omega$:

$$\frac{1}{\tau} = \frac{2.5}{\pi}\gamma^2\frac{\hbar\omega}{Mv^2}\,\frac{4}{3}\left(\frac{\alpha-\beta}{\alpha+\beta}\right)^2\omega\,. \tag{32}$$

This relaxation rate is related to the linewidth of the optical mode $\vec{q}=0$ in the first-order Raman spectrum. Both the magnitude and temperature dependence of observed linewidth are in accord with this theory.[6,13,14]

The same theory can now be used to obtain the interaction rate of an acoustic mode $\vec{q}$ interacting with another acoustic mode $\vec{q}'$ and an optic mode $\vec{q}''$. For simplicity let us assume that all optical modes $\vec{q}''$ have the same frequency ω_0, i.e., that the optical branch is completely flat. For a given mode $\vec{q}$, the locus of $\vec{q}'$ is given by the condition that $\omega' = \omega_0 - \omega$, that is a sphere for a simple Debye model. In the presence of a temperature gradient, the deviation of N' from equilibrium will vanish in the average. The optical mode will also be at equilibrium because of its vanishing group velocity and because it has the shortest relaxation time of all the modes. The occupation number factor in (9) thus becomes

$$[(N+1)(N'+1)N'' - NN'(N''+1)] = -n(N'-N_0)\,, \tag{33}$$

where N_0 is the equilibrium occupation of the optical mode, and N' that of the other acoustic mode, of frequency $\omega' = \omega_0 - \omega$. Substituting (30) into (9) and noting that

$$\sum_{\vec{q}'} = Ga^3(2\pi)^{-3}\int\frac{4\pi}{v}(q')^2\,d\omega'\,, \tag{34}$$

one obtains

$$\left(\frac{1}{\tau(\omega)}\right)_{\text{opt}} = \frac{32\pi^2\hbar\omega_0}{3Mv^3}\,\frac{a^3(q')^2}{(2\pi)^3}\omega\omega' \times\frac{2\gamma^2}{\sqrt{3}}\,\frac{\alpha-\beta}{\alpha+\beta}(N'-N_0)\,. \tag{35}$$

Since $q' = (\omega_0-\omega)/v = q_D(\omega_0-\omega)/\omega_D$, where $\omega_D = vq_D$ is the Debye frequency, and since $a^3q_D^3 = 6\pi^2$, one can rewrite (35) as

$$\left(\frac{1}{\tau(\omega)}\right)_{\text{opt}} = 7.3\gamma^2\frac{\hbar\omega_0}{Mv^2}\,\frac{\alpha-\beta}{\alpha+\beta}\left(\frac{\omega_0-\omega}{\omega_D}\right)^2 \times\frac{a}{v}\omega\omega'(N'-N_0)\,. \tag{36}$$

In the limit of high temperatures, when

$$N' - N_0 = (kT/\hbar\omega_0)\,\omega/\omega'\,, \tag{37}$$

Eq. (36) becomes

$$\left(\frac{1}{\tau(\omega)}\right)_{\text{opt}} = 7.3\gamma^2\frac{\alpha-\beta}{\alpha+\beta}\left(\frac{\omega_0-\omega}{\omega_D}\right)^2\frac{a}{v}\,\frac{kT}{Mv^2}\omega^2\,, \tag{38}$$

and the relaxation rate is thus comparable to that due to the interaction between acoustic modes, given by (21), but the frequency dependence is not quite the same at higher frequencies. The most important difference, however, is that the interaction cannot occur at all unless ω exceeds a minimum value of $\omega_0 - \omega_D$, or more generally $\omega_0 - \omega_1$, where ω_1 is the highest frequency of the acoustic branch.

The temperature dependence of the relaxation rate is governed by the factor $(N' - N_0)$ in (36). At low temperatures this behaves essentially as $e^{-\hbar\omega_1/kT}$, and thus varies as the Umklapp relaxation rate involving acoustic modes only. The interactions involving an optical mode have thus essentially the same temperature dependence both at low and at high temperatures as the interactions involving only acoustic modes.

That the relaxation rate (38) has the same temperature dependence and almost the same frequency dependence as the relaxation rate (21) due to acoustic modes only is in accord with the conclusions of Roufosse and Klemens,[11] who treated the same interactions on the extended zone picture and found the relaxation rate, summed over all interactions, to vary roughly as $\omega^2 T$.

However, this conclusion is at variance with numerical calculations of phonon lifetimes for KCl and NaCl performed by Logachev and Yurev,[15] and including interactions between acoustic and optical modes. High-frequency acoustic modes were found not to interact with optical modes, so that their lifetimes were relatively longer. This is in consequence of the vanishing of appropriate U-process matrix elements and the authors caution that this may be a special feature of that particular lattice. Qualitative arguments were advanced[16,17] to show how the temperature dependence of the thermal conductivity of germanium, silicon and various alkali halides might be explained in terms of these calculations.[15] It seems difficult to intercompare or reconcile their work with ours.

V. SUMMARY

An expression has been obtained for the relaxation rate due to four-phonon processes; its frequency and temperature dependence is given by (28); this is the same form as previously obtained by Pomeranchuk.[4] The magnitude of the interaction rate is much smaller than that due to three-phonon processes, even at the highest temperatures, so that these processes lead to a T^2 component in the thermal resistivity which is much smaller than observed. We have also obtained an expression for the relaxation rate of acoustic modes due to three-phonon interactions involving an optical mode. This relaxation rate is comparable, both in magnitude and temperature dependence, to the ordinary relaxation rate involving acoustic phonons only. Neither of these two processes will explain the temperature variation of the thermal resistance at high temperatures, which is found to be more rapid than linear.

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