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Thermal Conductivity of Complex Dielectric Crystals[*]

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The theory of the thermal resistivity of dielectric crystals at ordinary and high temperatures in terms of anharmonic three-phonon interactions is reformulated. The resistivity is similar in form to that obtained by Leibfried and Schlömann, but larger by a factor of 6.8. The theory is then extended to crystals where the unit cell contains many atoms. To include all three-phonon interactions one sums over all harmonics of the reciprocal-lattice vectors in an extended-zone representation. This sum increases the scattering rate. However, the matrix elements of the three-phonon processes are reduced in the case of large unit cells, because coherence is lost in the Fourier transform of the different bonds in each cell. A simplified model is chosen, and in this case the latter effect cancels the former, so that the anharmonic relaxation rate is substantially independent of the number of atoms per unit cell. However, the zone boundaries affect the phonon dispersion curves and reduce the group velocity of most modes. Using a model proposed by Slack, in which only the acoustic phonons of the fundamental zone contribute to the conductivity, and invoking the independence of the relaxation time with cell size here derived, the conductivity varies as the inverse cube root of the number of atoms per cell. The conductivity varies inversely with temperature, even if the phonon mean free path is shorter than the cell dimensions, because the major contribution to the anharmonic interaction comes from the highest harmonics of the fundamental reciprocal-lattice vectors.

INTRODUCTION

It was first pointed out by Debye[1] that the thermal resistivity of dielectric solids at ordinary temperatures arises from the scattering of lattice waves by fluctuations in the elastic constants which are due to thermal vibrations and to the fact that solids are not perfectly harmonic. This theory was put into its present form by Peierls,[2] who treated the lattice wave which is scattered on the same footing as the lattice wave which causes the scattering, and expressed the effects of anharmonicity in terms of three-phonon interactions. He pointed out the difference between three-phonon umklapp and normal processes. While the former cause thermal resistance, the latter can contribute to the resistivity indirectly. He showed that these processes lead to a thermal resistivity which is proportional to the absolute temperature at ordinary and elevated temperatures, as in the Debye theory, and in agreement with observations on many dielectric crystals.[3]

Peierls's theory has been the basis of almost all subsequent theoretical work. Pomeranchuk[4] considered the question of low-frequency divergencies and invoked quartic anharmonicities to remove their effect at high temperatures. Other investigations[5,6] dealt with the effects of imperfections on the thermal conductivity, important primarily at low temperatures. All this early work was semiquantitative; its conclusions and the comparison with experiments stressed the temperature dependence of the thermal resistivity rather than its magnitude. The magnitude of the intrinsic thermal resistivity was first treated by Leibfried and Schlömann,[7] that of the defect-induced resistivity by Klemens.[8]

Leibfried and Schlömann's quantitative theory[7] of the intrinsic thermal resistivity due to umklapp process, particularly at high temperatures, is based on Peierls's perturbation formalism for three-phonon processes, but includes an estimate of the strength of the interaction. It also takes explicit account of the crystal structure or the corresponding zone structure to estimate the umklapp processes. To account for the normal processes, i.e., to properly solve the Boltzmann equation, the authors developed a variational method, which in their form is equivalent to a phonon momentum balance subsequently used by Ziman.[9] The formula they derived for the high-temperature thermal conductivity has since been used as a standard expression against which much experimental data has been compared.

The present paper will consider some unsolved questions. The most trivial of these is the numerical reliability of the Leibfried-Schlömann formula. This depends on the choice of the perturbation Hamiltonian. We shall use the estimate of Klemens,[10] which appears to give better results for the related problem of anharmonic phonon scattering by static strain fields. The main purpose of the present paper, however, is to attempt to treat the influence of crystal structure, and to investigate the limits of validity of the reciprocal temperature dependence of the thermal conductivity, which all versions of the Peierls theory predict at elevated temperatures.

We shall see that as long as only cubic anharmonicities need to be considered, and provided the crystal is free of imperfections, the $1/T$ variation of the thermal conductivity should persist even if the temperature is high enough and the crystal structure complex enough that the repeat distance is comparable to or larger than the phonon mean free path.

The present extension of the theory may thus prove useful not only to explain existing experimental data—which is in any case sometimes of doubtful validity at elevated temperatures—but more importantly to extrapolate thermal-conductivity data to higher temperatures, where measurements are difficult and good data scarce.

THREE-PHONON INTERACTIONS

Following the notations of Ref. 10 one can write the unperturbed Hamiltonian, corresponding to the structurally perfect and completely harmonic crystal, as

$$H^0 = \sum_{\vec{q},j} \frac{1}{2} M \,\omega^2(\vec{q},j)[a^\dagger(\vec{q},j)\,a(\vec{q},j) + a(\vec{q},j)\,a^\dagger(\vec{q},j)] \;. \tag{1}$$

$\vec{q}$ and ω are the wave vector and frequency of a lattice wave of polarization index j, M is the mass of a unit cell, and $a^\dagger$ and a are the phonon creation and annihilation operators of the dimension of displacement and are explicitly given by

$$\begin{aligned} a_{N,N-1} &= (\hbar/M\omega)^{1/2} N^{1/2} \;, \\ a^\dagger_{N,N+1} &= (\hbar/M\omega)^{1/2} (N+1)^{1/2} \;, \end{aligned} \tag{2}$$

where N is the number of phonons in a mode. The perturbation Hamiltonian due to cubic anharmonicities can be expressed in the form

$$H' = \sum_{\vec{q},\vec{q}\,',\vec{q}\,''} C_3(\vec{q},\vec{q}\,',\vec{q}\,'')\,a(\vec{q}),\; a^\dagger(\vec{q}\,')\,a^\dagger(\vec{q}\,'') \;, \tag{3}$$

where the summation extends over all triplets of normal modes, including cases where creation and annihilation operators are interchanged, and where the polarization index is understood to be included in the specification of modes $\vec{q}$, etc. From the regularity of the crystal lattice and the fact that all unit cells contribute to H' it follows that the coefficient $C_3(\vec{q},\vec{q}\,',\vec{q}\,'')$ vanishes unless the wave vectors of the three participating modes satisfy an interference condition of the form

$$\vec{q} + \vec{b} = \vec{q}\,' + \vec{q}\,'' \;, \tag{4}$$

where $\vec{b}$ is a reciprocal-lattice vector. Processes of the type $\vec{b} = 0$ are normal processes; other processes are umklapp processes.

The rate of change of the number of phonons N in mode $\vec{q}$ is given by time-dependent perturbation theory

$$t\,\frac{dN}{dt} = \sum_{\vec{q}\,',\vec{q}\,''} 2\,|C_3|^2 \frac{\hbar^3}{M^3\omega\omega'\omega''}\;\frac{1-\cos\Delta\omega t}{\hbar^2\Delta\omega^2}$$

$$\times[(N+1)N'N''-N(N'+1)(N''+1)]\,, \tag{5}$$

where

$$\Delta\omega=\omega-\omega'-\omega''\,. \tag{6}$$

In the above summation, different polarizations must be included. The possibility of phonon $\vec{q}$ combining with $\vec{q}\,'$ to form a phonon $\vec{q}\,''$ must also be included by changing the sign of ω' and interchanging the factors N' and $N'+1$.

The average occupation number of each mode $\vec{q}$ is now obtained from the Boltzmann equation describing the steady state in the presence of a temperature gradient; i.e.,

$$\left(\frac{dN}{dt}\right)_{\rm int}+\left(\frac{dN}{dt}\right)_{\nabla T}=0\,. \tag{7}$$

This balances the rate of change due to interactions and the rate of change due to a temperature gradient ∇T. The rate of change due to interactions depends on the departure of the average occupation number of the various modes from thermal equilibrium. Let this departure be $n(\vec{q})$ for mode $\vec{q}$, etc. To a good approximation, $(dN/dt)_{\rm int}$ is linear in n, n', and n'', the deviation of the modes participating in (5). All these deviations are proportional to ∇T and, in the steady state, n'/n, n''/n, etc., form definable ratios. One can thus define an effective relaxation time $\tau(\vec{q})$ for each normal mode by

$$\left(\frac{dN}{dt}\right)_{\rm int}=-\frac{n}{\tau}\,. \tag{8}$$

Substituting this into (7), n is formally proportional to τ. From this solution of the Boltzmann equation one can obtain the heat current and finally the thermal conductivity κ. One finds in terms of Cartesian components, l, n:

$$\kappa=\sum_{\vec{q}}\tau v_l v_n C(\vec{q}) \tag{9}$$

or, disregarding the anisotropy of the thermal conductivity,

$$\kappa=\tfrac{1}{3}\int\tau v^2 C(\omega)\,d\omega\,, \tag{10}$$

where $C(\vec{q})$ is the contribution of mode $\vec{q}$ to the specific heat and $C(\omega)\,d\omega$ the contribution to the specific heat per unit volume of modes in the frequency interval ω, $d\omega$.

APPROXIMATE EVALUATION OF RELAXATION TIME

The perturbation Hamiltonian is given by Eq. (3). The coefficient C_3 depends on the nature of the anharmonic forces. An extension of the Grüneisen model to the case when the dilatation is inhomogeneous leads to the following expression[10]:

$$C_3=[2\gamma/(3G)^{1/2}]Mv^2 q\,q'\,q''\,, \tag{11}$$

where γ is the Grüneisen constant. The coefficient C_3 is given by (11) provided (4) is satisfied; it vanishes otherwise.

Substituting (11) into (5) one obtains

$$t\frac{dN}{dt}=\sum_{\vec{q}\,',\vec{b},j',j''}\frac{8\gamma^2}{3G}\frac{\hbar}{Mv^2}\,\omega\,\omega'\,\omega''\,\frac{1-\cos\Delta\omega t}{\Delta\omega^2}$$

$$\times[(N+1)N'N''-N(N'+1)(N''+1)]\,. \tag{12}$$

The summation extends over all $\vec{b}$ and $\vec{q}\,'$ with $\vec{q}\,''$ given by (4). It also extends over all polarizations of $\vec{q}\,'$ and $\vec{q}\,''$, subject, however, to the restriction implied by $\Delta\omega=0$. This is because the resonance factor $(1-\cos\Delta\omega t)/\Delta\omega^2$ restricts the significant contributions to interactions for which $\Delta\omega=0$. This condition, together with (4), forces all contributing triplets to be such that $\vec{q}\,'$ lies on a surface or a set of surfaces which in the isotropic continuum are surfaces of revolution about $\vec{q}+\vec{b}$. Since there are three different values for j′ and j″, there will be nine such surfaces (only four distinct ones in an isotropic continuum), but some of these surfaces will not be real.

For example, if $\vec{q}$ decays into two phonons $\vec{q}\,'$ and $\vec{q}\,''$ and if $\vec{q}$ is longitudinal, the locus of $\vec{q}\,'$ will be an ellipsoid of revolution if $\vec{q}\,'$ and $\vec{q}\,''$ are both transverse, and a more complex set of figures[11] if one is transverse and the other longitudinal.

The summation over $\vec{q}\,'$ in (12) can be replaced by an integration

$$\sum_{\vec{q}\,'}\rightarrow\frac{Ga^3}{(2\pi)^3}\int dS'\,(|\nabla_{\vec{q}\,'}\Delta\omega|)^{-1}\,d(\Delta\omega)\,, \tag{13}$$

where a^3 is the atomic volume and dS' is an element of the surface $\Delta\omega=0$ in $\vec{q}\,'$ space. If $\vec{q}$ is longitudinal and $\vec{q}\,'$ and $\vec{q}\,''$ transverse, the summation over j' and j'' introduces a factor of 4. The integration of the resonance factor over $\Delta\omega$ introduces a factor πt.

Let us assume for simplicity that all modes are occupied by their equilibrium number of phonons $N^0(\vec{q}\,')$, etc., except for the mode $\vec{q}$ under investigation for which

$$N(\vec{q})=N^0(\vec{q})+n(\vec{q})\,. \tag{14}$$

Substituting into the factor in (12) enclosed in square brackets, then all terms independent of n, the deviation from equilibrium, vanish for each interacting triplet. This is a consequence of the form of N^0 together with the requirement that $\Delta\omega=0$. The remaining terms in the square brackets can be written

$$(N+1)N'N''-N(N'+1)(N''+1)$$

$$=-n(\vec{q})[N^0(\vec{q}\,')+N^0(\vec{q}\,'')+1]\,. \tag{15}$$

Now, because $\Delta\omega=0$ and $N^0=(e^x-1)^{-1}$, where $x=\hbar\omega/KT$ (K is the Boltzmann constant),

$$N^0(q') + N^0(q'') + 1 = N^0(\vec{q}')\, N^0(\vec{q}'')/N^0(\vec{q}) \;, \tag{16}$$

and in the high-temperature limit, this expression can be approximated by $KT\omega/\hbar\, \omega'\omega''$.

Dividing (12) by nt to get the relaxation rate as defined by (8), one obtains the inverse of the "relaxation time of a single mode," i.e., the expression obtained assuming that n' and n'' vanish or at least vanish in the average.

Finally, since the relaxation rate (12) involves a summation over all $\vec{q}'$, it will depend on the nature of the locus of all $\vec{q}'$ which satisfy $\Delta\omega = 0$ and the wave-vector relation (4). This dependence arises from (13). In general, the loci of $\vec{q}'$ are complicated. In an isotropic continuum, they would be surfaces of revolution about $\vec{q}$. If the zone structure did not modify the dispersion relations, they would be surfaces of revolution about $\vec{q}+\vec{b}$. In the simple case of a process where a longitudinal mode $\vec{q}$ decays into two transverse modes, the locus is an ellipsoid of revolution.[11] This, in turn, may be approximated by a sphere.

In order to obtain a rough estimate of the relaxation rate, and in order to obtain an estimate of the effectiveness of the different umklapp processes, each associated with a reciprocal-lattice vector $\vec{b}$, we shall make the following assumptions: (i) The locus of $\vec{q}'$ is replaced by a sphere of radius $\frac{1}{2}|\vec{q}+\vec{b}|$ for each value of $\vec{b}$. (ii) The summation over j' and j'' introduces a factor of 4. (iii) The value of $|\nabla_{\vec{q}'}(\Delta\omega)|$ occurring in the integrand of (13) is replaced by $\sqrt{2}v$; this corresponds to the value at the points of the ellipsoid where the projection of $\vec{q}'$ and $\vec{q}''$ on $(\vec{q}+\vec{b})$ are equal in magnitude. The summation (13) can thus be approximated by

$$\sum_{\vec{q}',j',j''} \rightarrow \frac{4Ga^3}{(2\pi)^3}\, 4\pi \frac{(\vec{q}+\vec{b})^2}{4}\, \frac{1}{\sqrt{2}v} \int d\Delta\omega \;. \tag{17}$$

Substituting this into (12), integrating over the resonance factor, and using (15) and (16), one finally obtains the following expression for the single-mode relaxation rate:

$$\frac{1}{\tau} = \sum_{\vec{b}} \frac{a^3}{3\pi\sqrt{2}}\, \frac{KT}{Mv^2}\, \frac{\omega^2}{v} \left|\vec{q}+\vec{b}\right|^2 , \tag{18}$$

where the summation extends over all reciprocal-lattice vectors.

If we require that $\vec{q}'$ and $\vec{q}''$ belong to the fundamental zone then we must consider three different $\vec{b}$ vectors in the summation over all umklapp processes. In a simple cubic lattice, all $\vec{b}$'s have the same magnitude $2\pi/a$, where a^3 is the volume of the unit cell. Neglecting cross terms when averaging over all angles between $\vec{q}$ and $\vec{b}$, we write

$$|\vec{q}+\vec{b}|^2 = q^2 + 4\pi^2/a^2 \;. \tag{19}$$

If we further neglect q^2 relative to b^2, we can write, in place of (18),

$$1/\tau = A\omega^2 T \;, \tag{20a}$$

where

$$A = (4\pi/\sqrt{2})(a/v)\, \gamma^2 K/Mv^2 \;. \tag{20b}$$

HIGH-TEMPERATURE THERMAL CONDUCTIVITY

If we identify τ of (20) with the relaxation time in the expression for the conductivity [Eq. (10)], we obtain at elevated temperatures, where

$$C(\omega) = 3K\omega^2/2\pi^2 v^3 \;, \tag{21}$$

the following expression for the thermal conductivity:

$$\kappa = \frac{3}{4\pi^3\sqrt{2}}\, \frac{Mv^2}{\gamma^2}\, \frac{\omega_D}{a}\, \frac{1}{T} \;, \tag{22}$$

where ω_D is the Debye frequency. We may compare this with the expression obtained by Leibfried and Schlömann,[7] incorporating a correction of a numerical error as noted by Julian[12]:

$$\kappa = \frac{24}{20}\, \frac{(4)^{1/3}}{\gamma^2}\, \frac{K^3}{(2\pi)^3\hbar^3}\, Ma\Theta^2 \frac{\Theta}{T} \;. \tag{23}$$

Using the relation $v^2/a^2 = \omega_D^2/(6\pi^2)^{2/3}$, we can rewrite our present result in the form

$$\kappa = \frac{3^{1/3}}{2^{1/6}\pi^{4/3}\gamma^2}\, \frac{K^3}{(2\pi)^3\hbar^3}\, Ma\Theta^2 \frac{\Theta}{T} \;, \tag{22$'$}$$

so that the conductivity given by (22) and (23) is in the ratio 1 to 6.8. Some of this discrepancy can be traced to basic differences in the calculations. Leibfried and Schlömann used an interaction Hamiltonian for three-phonon interactions which differs by a factor of 4 from the one used here[10]; this should increase their conductivity relative to (22) by a factor of 16. On the other hand, they took account of normal processes by a variational method, while (22) was obtained by identifying τ with the single-mode relaxation time. This decreases their conductivity relative to (22). If $1/\tau$ is proportional to ω^2 and $T > \Theta$, one can readily see that the two methods yield conductivities in the ratio

$$\left(\int_0^{\Theta/T} x^4\, dx\right)\left(\int_\Theta^{\Theta/T} dx\right)\left(\int_0^{\Theta/T} x^2\, dx\right)^{-2} = \tfrac{9}{5} \;, \tag{24}$$

with the variational method yielding the lower conductivity. All other factors being equal, one would thus expect Leibfried and Schlömann's estimate of the conductivity to exceed the present one by a factor of $16 \times \frac{5}{9} = 8.9$. The actual discrepancy between (23) and (22′) is only 6.8. The remaining factor of 1.3 must be attributed to differences in the approximations made in the summation over all $\vec{q}'$ [Eqs. (13) and (17)]. Considering the nature of these approximations, the disagreement between the two methods is not too serious.

EFFECTS OF CRYSTAL STRUCTURE

We have assumed, so far, that the crystal structure is simple cubic, while Leibfried and Schlömann based their calculations on a face-centered-cubic lattice. The crystal structure determines the position of the zone boundaries in reciprocal space. The introduction of additional zone boundaries has two effects. First, they modify the phonon dispersion curve in an appreciable fraction of reciprocal space, and hence the phonon group velocities. Second, they give rise to additional umklapp processes, leading to a shorter relaxation time due to anharmonic processes. This effect is complicated by the modification of the dispersion curves, which modify the loci of interacting mode $\vec{q}'$ in the summation (13). This makes the proper treatment of the lattice thermal conductivity of complex crystals a formidable undertaking.

Slack[13] simplified this problem by assuming that the group velocity of all nonacoustical modes is sufficiently small so that their contribution to the thermal conductivity can be neglected. Only the acoustical modes in the fundamental zone are considered to contribute. This is a good approximation if the different atoms in each unit cell have masses which differ substantially or if the bonds differ substantially, so that the new zone boundaries lead to wide gaps in the dispersion curves. Based on this assumption, the following argument yields the variation of thermal conductivity with the size of the unit cell.

One can define a reduced Debye temperature Θ_c related to the velocity of sound and the volume of the fundamental zone analogously to the Debye temperature Θ which is related to the volume of the extended zone, defined for a unit cell containing one atom. If the unit cell contains N atoms, then

$$\Theta_c = \Theta / N^{1/3} . \qquad (25)$$

Substituting (20) into (10) with $C(\omega)$ given by (21), but with the integral cutoff at a frequency $K\Theta_c/\hbar$, we obtain

$$\kappa_c / \kappa_0 = \Theta_c / \Theta = N^{-1/3} , \qquad (26)$$

where κ_0 is the conductivity given by (22). This variation with the size of the unit cell seems roughly borne out by Slack's measurements. On the other hand, it may be argued that the relaxation time itself decreases with increasing N; in that case one should expect a somewhat more rapid variation with cell size. A simple scaling of the parameters $a\Theta^3$ in (23) would lead to a variation of the conductivity as $N^{-2/3}$.

We shall now investigate the effect of the additional zone boundaries on the relaxation time itself. We shall assume that the additional zone boundaries introduce additional scattering processes, and that this tends to shorten the relaxation time. We shall disregard the fact that the changes in the dispersion relations due to the zone boundaries tend to change the loci in $\vec{q}'$ space of the allowed interactions. Our model thus applies mainly to complex crystals where all atoms have the same or similar mass, and where differences in the various bonds and in their orientations affect the anharmonic components more than the harmonic components.

Let us consider a complex dielectric crystal containing N atoms per unit cell. Let us further assume that within each cell the positions of the various atoms follow some random pattern, but that this pattern is, of course, reproduced from cell to cell. Because the unit cell is now larger, a new set of reciprocal lattice vectors can now be defined by

$$b_i = (2\pi / N_i a_i) n_i , \qquad (27)$$

where $N_i a_i$ is one of the linear dimensions of the new unit cell $N_1 N_2 N_3 = N$, and n_i is an integer ranging from 0 to N_i. For simplicity we shall choose $N_1 = N_2 = N_3 = \mathfrak{N} = N^{1/3}$, and also $a_1 = a_2 = a_3 = a$. Two modifications must therefore be made to the previous theory:

The interaction matrix element must be recalculated, taking into account the spatial distribution of the anharmonic bonds within the unit cell.

The summation appearing in Eq. (18) must be extended to include all reciprocal-lattice vectors defined by (27).

The matrix element can be approximated as follows. Analogously to (11) we express C_3 in the form

$$C_3 = \frac{2\gamma}{\sqrt{3G}} \, M v^2 q q' q'' \frac{1}{G_0} \sum_{\text{atoms}} e^{i(\vec{q} - \vec{q}' - \vec{q}'') \cdot \vec{x}} , \qquad (28)$$

where $\vec{x}$ is an atomic site, and the sum is over all atoms in the crystal. Let there be G_0 atoms in the crystal, and $G_0 = NG$, where G is the number of cells and N the number of atoms in each cell. The sum over all atoms can now be broken up into a sum over all unit cells, and a sum over all sites in each unit cell, i.e.,

$$\sum_{\text{atoms}} e^{i(\vec{q} - \vec{q}' - \vec{q}'') \cdot \vec{x}} = \sum_{\text{cells}} \sum_{\text{sites}} e^{i(\vec{q} - \vec{q}' - \vec{q}'') \cdot (\vec{X} + \vec{r})} , \qquad (29)$$

where $\vec{X}$ denotes the coordinate of a cell and $\vec{r}$ denotes a coordinate of an atomic site in the cell. From the summation over cells or $\vec{X}$ we obtain, as before, that C_3 vanishes unless the interference condition (4) is satisfied. For processes of reciprocal-lattice vector $\vec{b}$ the matrix element C_3 will contain the factor

$$C_3(\vec{b}) \propto \sum_{\vec{r}} e^{-i\vec{b} \cdot \vec{r}} \qquad (30)$$

in the approximation which gives equal weight to all atom sites. This expression can readily be generalized to the case where different sites have associated bonds of different degree of anharmonicity. The present approximation has the virtue that it yields the same result as we had for a monatomic lattice in the case $\vec{b}=0$ (normal processes), and leads to the same Grüneisen hypothesis in the case when $q\rightarrow 0$. More generally, $C_3(\vec{b})$ is given by the $\vec{b}$th Fourier component of the spatial distribution of the anharmonicity.

Although in principle each crystal structure must be Fourier inverted to get the matrix elements, so that the structural details of each solid must be fully considered, we shall attempt to understand general trends by making the approximation that the positions of the atoms in the unit cell form a random array. This array must of course be faithfully repeated from cell to cell. Thus the sum over $\vec{r}$ in (30) consists of N terms, each of the same magnitude, but with a random-phase factor. This sum thus behaves like the square root of N, or rather its square in $|C_3|^2$ behaves as N. Thus the term $|C_3|^2$ appearing in the relaxation rate will be reduced, relative to the value for a monatomic crystal, by a factor N. We thus have, in place of Eq. (18), the following expression for the relaxation rate:

$$\frac{1}{\tau}=\sum_{\vec{b}}\frac{a^3}{3\pi\sqrt{2}}\,\frac{KT}{Mv^2}\,\frac{\gamma^2\omega^2}{vN}\,|\vec{q}+\vec{b}|^2\,. \qquad (31)$$

As a first step, we shall consider that the wave number q is smaller than all reciprocal-lattice vectors and focus our attention upon the summation over all reciprocal-lattice vectors neglecting $\vec{q}$. Replacing $\vec{b}$ by (27) in the expression for the relaxation rate, we can derive

$$\frac{1}{\tau}=\frac{a^3}{3\pi\sqrt{2}}\,\frac{KT}{Mv^2}\,\frac{\gamma^2\omega^2}{vN}\,\frac{4\pi^2}{\mathfrak{N}^2a^2}\sum_{n_i}(n_i)^2\,. \qquad (32)$$

This summation can be carried out explicitly only for small values of n_i; i.e., when the number of atoms per unit cell is small. In the case of one atom per unit cell, the only three possibilities are $n_1=1$, $n_2=0$, $n_3=0$, and the two others are found by cyclic permutations. Therefore

$$\frac{1}{N}\,\frac{4\pi^2}{N^{2/3}a^2}\sum n_i^2=\frac{12\pi^2}{a^2}\,. \qquad (33)$$

When $N=8$, the contributions for a hemisphere amount to

$$\frac{1}{N}\,\frac{4\pi^2}{N^{2/3}a^2}\sum n_i^2=\frac{39\pi^2}{8a^2}\simeq\frac{5\pi^2}{a^2}\,. \qquad (34)$$

When $N=27$, we have

$$\frac{1}{N}\,\frac{4\pi^2}{N^{2/3}a^2}\sum n_i^2=\frac{6\pi^2}{a^2}\,. \qquad (35)$$

When $N=64$, we have

$$\frac{1}{N}\,\frac{4\pi^2}{N^{2/3}a^2}\sum n_i^2=\frac{7\pi^2}{a^2}\,. \qquad (36)$$

When $N=125$, we have

$$\frac{1}{N}\,\frac{4\pi^2}{N^{2/3}a^2}\sum n_i^2=\frac{8\pi^2}{a^2}\,. \qquad (37)$$

On another hand, where the number of atoms per unit cell becomes large, we can replace the summation over reciprocal-lattice vectors by an integration

$$\sum_{\vec{b}} b^2\rightarrow 4\pi\int_0^B\frac{b^4}{b_0^3}\,db\,, \qquad (38)$$

where B is defined by

$$\tfrac{4}{3}\pi B^3/b_0^3=4N \qquad (39)$$

and b_0 by

$$b_0^2=4\pi^2/N^{2/3}a^2\,. \qquad (40)$$

The summation is thus equivalent to

$$\frac{4\pi^2}{a^2}N\,\frac{12}{5}\left(\frac{3}{\pi}\right)^{2/3}\simeq\frac{9\pi^2}{a^2}N\,, \qquad (41)$$

and the relaxation rate (32) can be written

$$\frac{1}{\tau}=\frac{a^3}{3\pi\sqrt{2}}\,\frac{KT}{Mv^2}\,\frac{\gamma^2\omega^2}{v}\,\frac{9\pi^2}{a^2} \qquad (42)$$

or in the form $1/\tau=A'\omega^2T$, where

$$A'=(3\pi/\sqrt{2})\,(a/v)\,\gamma^2\,K/Mv^2\,. \qquad (43)$$

The coefficient A' is thus substantially independent of the number of atoms per unit cell, and about $\frac{3}{4}$ of the value of A of Eq. (20b). This independence is due to the cancellation of two factors. The summation over all reciprocal-lattice vectors increases the relaxation rate by a factor N, the number of atoms per unit cell. However, the anharmonic matrix element C_3 is reduced because the unit cell is enlarged. In the case of one atom per unit cell, each atom site contributes coherently to the $\vec{b}$th Fourier component of the anharmonicity. In the present case, however, each group of N atoms contributes incoherently, even though there is constructive interference between the contributions from each such group or unit cell. This reduces $|C_3|^2$ by a factor N, compensating for the increase due to the sum over all zone boundaries. Note that a in (43) is defined by letting a^3 be the volume per atom; this quantity is less variable among solids than the volume per unit cell. The latter is Na^3 in our notation.

We can turn to the quantity $\vec{q}$ neglected in (31) and study how it can affect the relaxation rate. We can see that the term $\sum_{\vec{b}}(q^2+b^2)$ appearing in the relaxation rate will behave as

$$q^2\mathfrak{N}^2+\frac{4\pi^2}{\mathfrak{N}^2a^2}\,\frac{\mathfrak{N}^5}{5}\,3\left(\frac{3}{4\pi}\right)^{2/3} . \qquad (44)$$

In the limiting case where q becomes large, only those reciprocal-lattice vectors $\vec{b}$ which are of comparable magnitude need be counted in the summation. All smaller $\vec{b}$'s can be neglected without appreciable effect. Taking into account the numerical factor $\frac{3}{5}$ it can be deduced that all $\vec{b}$'s whose magnitude is smaller than $1.3q$ will not participate significantly in the summation. However in the case of extremely large q, where all $\vec{b}$'s could be neglected in the summation, the result would be affected by a factor of $\frac{5}{3}$ at most.

In intermediate cases both q and b must be included in the expression for the relaxation rate and the thermal conductivity. The relaxation rate is written

$$\frac{1}{\tau}=A'\omega^2\left[\frac{5}{3}\,\frac{q^2a^2}{4\pi^2}\left(\frac{4\pi}{3}\right)^{2/3}+1\right] . \qquad (45)$$

The thermal conductivity given by (10), making use of (21) for $C(\omega)$, becomes

$$\kappa=\frac{3K}{2\pi^2vA'T}\int_0^{\omega_D}\left[\frac{5}{3}\,\frac{\omega^2a^2}{4\pi^2v^2}\left(\frac{4\pi}{3}\right)^{2/3}+1\right]^{-1}d\omega \qquad (46)$$

or

$$\kappa=\frac{3K}{2\pi^2vA'T}\tan^{-1}\left(\frac{5}{3}\right)^{1/2}\left(\frac{4\pi}{3}\right)^{1/3}\frac{\omega_Da}{2\pi v} . \qquad (47)$$

Making use of the relation $q_D^3a^3=6\pi^2$, we find that $\tan^{-1}\sqrt{\frac{5}{3}}(\frac{4}{3}\pi)^{1/3}\,\omega_Da/2\pi v\simeq 0.67$ while the value of the argument was 0.81. This would therefore produce a slight decrease of the thermal conductivity.

HIGH-TEMPERATURE EFFECTS ON THE THERMAL CONDUCTIVITY

At high temperatures, the resonant factor $1-(\cos\Delta\omega t)/\Delta\omega^2$ has a finite thickness in $\vec{q}\,'$ space and consequently the range of $\Delta\omega$ is restricted. The inner limit will be determined by the size of the locus

$$\Delta\omega_{\text{in}}=\tfrac{1}{2}\,|(\vec{q}+\vec{b})|\,v . \qquad (48)$$

The external limit will be determined by the magnitude of the reciprocal-lattice vector. For the sake of symmetry we choose

$$\Delta\omega_{\text{out}}=\tfrac{1}{2}\,|\vec{q}+\vec{b}|\,v . \qquad (49)$$

Consequently, the relaxation rate is proportional to

$$I=\int_{-1/2|\vec{q}+\vec{b}|v}^{+1/2|\vec{q}+\vec{b}|v}\frac{1-\cos\Delta\omega t}{\Delta\omega^2}\,d(\Delta\omega) . \qquad (50)$$

The time can be replaced by the first-order approximation for the relaxation time $\tau_0=(A\omega^2T)^{-1}$. The integral cannot be calculated exactly. It will be approximated as follows.

In the case of very large integration limits, we let $\Delta\omega$ vary from minus to plus infinity. Then

$$I=\pi\tau_0 . \qquad (51)$$

In the case of very small integration limits, we can develop the integrand in Taylor series keeping only first-order terms. Then

$$I=\tfrac{1}{2}\,|\vec{q}+\vec{b}|\,v\tau_0^2 . \qquad (52)$$

Intermediate cases can be treated by joining smoothly these two extreme behaviors. The inverse-tangent function is best suited to such interpolation. Then

$$I=2\tau_0\tan^{-1}(\tfrac{1}{4}\,|\vec{q}+\vec{b}|\,v\tau_0) . \qquad (53)$$

In the case of complex dielectric crystals, zone structure has been taken into account by summing over all participating reciprocal-lattice vectors. At high temperature, not all reciprocal-lattice vectors will participate in the summation. We must disregard all loci whose dimensions are smaller than or equal to their thickness. Thus all loci whose radii $\frac{1}{2}|\vec{q}+\vec{b}|$ are smaller or equal to $\Delta\omega/v=(A\omega^2/v)T$ must be rejected. However, due to the factor b^5 appearing in the summation (38) which determines the relaxation rate, the exclusion of the few smaller loci will not lead to a significant change.

SUMMARY

We therefore arrive at the following conclusions.

When one considers a complex dielectric crystal it is impossible to make any well-defined predictions about the matrix elements unless one knows the exact structure of the crystal under consideration. A statistical distribution of atoms within a unit cell has been chosen as a simplification; this leads to a matrix element inversely proportional to the square root of the number of atoms contained in the unit cell. The relaxation rate, on the other hand, will also include a summation over all reciprocal-lattice vectors. These factors tend to cancel and when the number of atoms per unit cell increases, the relaxation rate and therefore the resistivity increase slightly at first and then tend towards a constant independent of the number of atoms per unit cell.

On the other hand, one must also consider the effect of the zone boundaries on the group velocity of the modes. Using the model of Slack,[14] who disregarded the contribution of all modes except the fundamental acoustical modes to the thermal conductivity, one finds that the thermal conductivity varies inversely as the cube root of N, the number of atoms per unit cell [see Eq. (26)]. This result was based on the assumption that the anharmonic relaxation rate is independent of N; we now see that this assumption is roughly justified.

The second part of this work deals with the effects of elevated temperatures upon the thermal resistivity of complex crystals. Theoretically, it is understood that a locus will participate in the summation over reciprocal-lattice vector only when its thickness does not exceed its size. Practically, however, this effect is not dramatic owing to the fact that the summation over reciprocal-lattice vectors can be replaced by an integral which diverges like b^5. Consequently, if the lower limit of integration is replaced by $b_{\min}$ defined by $A\omega^2T/v$ instead of zero, no net effect will be observed.

Early work by Eucken[3,14] pointed towards a departure from the $1/T$ dependence of the thermal conductivity at elevated temperatures. We conclude that this should not be an intrinsic effect. For example, experimental thermal-conductivity curves of naphthalene by Lees[15] showed a weak temperature dependence, not inconsistent with $\kappa \propto T^{-1/2}$. However, recent work on naphthalene,[16] as well as an earlier measurement,[3] shows that the thermal resistivity is directly proportional to temperature. The weak temperature dependence observed by Lees is now believed to be due to defects. We now expect that in structurally perfect crystals the $1/T$ dependence should hold until the temperature is high enough so that the phonon mean free path is short enough to approach interatomic distances. At those temperatures, however, the melting point has been exceeded in most cases.[7]

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Electron Localization and Atomic Correlation in One-Dimensional Disordered Systems*†

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The author reports fairly extensive new investigations of the electronic structure of one-dimensional disordered systems. A formalism is developed in the tight-binding approximation that includes nearest-neighbor correlation. This formalism is used to calculate density of states and two kinds of localization lengths for several model systems. In the uncorrelated binary alloy good agreement is found with Monte Carlo calculations performed recently by Bush. The results in the study of the disorder-induced metal-nonmetal transition confirm the model of Cohen and Sak.

I. INTRODUCTION

One-dimensional disordered systems have been extensively studied for the last two decades. The propagation of phonons as well as electrons in one-dimensional random chains and lattices have occupied many researchers, such as Dyson, Mott, Borland, and Hori *et al.*[1,2] In almost all cases, the problem was treated in the framework of a single-particle Hamiltonian with random potential. The problem has been of relatively little physical interest, because many of the results were true only for one dimension, and therefore were of little use for real physical systems. Recently, however, the problem acquired considerable physical importance after the discovery and experimental study of a number of very interesting solids.[3,4] These solids consist of long conducting stacks of planar organic or metallo-organic ions. These stacks interact very weakly with each other. The propagation of electrons is thus largely confined to individual stacks and is nearly one dimensional. Many