PHYSICAL REVIEW B VOLUME 48, NUMBER 9 1 SEPTEMBER 1993-I

Anharmonic thermal resistivity of dielectric crystals at low temperatures

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(Received 16 February 1993)

The intrinsic thermal resistance of dielectric crystals at low temperatures due to three-phonon Umklapp processes has been treated theoretically, taking account of the restrictions imposed by wave-vector selection and frequency conservation rules, as well as the known phonon-dispersion curves. Since low-frequency phonons cannot interact directly with zone-boundary phonons, the transfer of excess momentum takes place in two steps: a normal process with modes of intermediate frequency, followed by an Umklapp process of intermediate-frequency phonons with phonons near the zone boundary of two different polarization branches with different frequencies. The intermediate frequency is given by that frequency difference. The second step can also be scattering by point defects, so that the apparent Umklapp resistance can be modified by point defects, which scatter the intermediate-frequency phonons much more strongly than the thermal phonons. The important processes in different frequency ranges depend on the dispersion curves and on the residual point defects; various cases are discussed. The theory has only one adjustable parameter, the Grüneisen constant. The point-defect scattering strength is deduced from the departures of the thermal conductivity in the boundary scattering regime at very low temperatures from a T^3 dependence. The theory has been compared to measurements on LiF, NaF, diamond, Si, and enriched ^{74}Ge. Reasonably good agreement with experimental data can be obtained without invoking an adjustable exponent in the Umklapp resistance.

I. INTRODUCTION

The intrinsic thermal conductivity of dielectric crystals is controlled by three-phonon Umklapp processes, i.e., processes in which the sum of the wave vectors is not conserved but changes by a reciprocal-lattice vector.

For thermal modes at low temperature to participate in such a process, the thermal mode of frequency $\omega \sim kT/\hbar$, must combine with a mode near the zone boundary of frequency ω_z. This requires the prior presence of a phonon in that mode, and at low temperature this has a low probability of the order $\exp(-\hbar\omega_z/kT)$. Peierls[1] thus predicted that the intrinsic thermal conductivity should vary as $\exp(\Theta'/T)$ where Θ' is an exponent of the order of the Debye temperature Θ. In Peierls' pioneering work Θ' was not specified further.

Subsequent workers[2] have assumed that $k\Theta' = \hbar\omega_z$, where ω_z is the frequency of the lowest-frequency mode at a zone boundary. Leibfried and Schlömann[3] attempted in this way to obtain an estimate of the intrinsic low-temperature thermal conductivity, and noted that this attempt did not agree with such observations as then existed. This contrasted with their results at temperatures near or above Θ, where their analysis produced conductivity values in good agreement with data. How good that agreement has since turned out to be is evident from a later review by Slack.[4]

At low temperatures the intrinsic Umklapp or U processes act in combination with boundary scattering, with point-defect scattering, and with three-phonon "normal" processes, i.e., processes which conserve the phonon wave vector (N processes). The N processes play a different and indirect role in producing thermal resistance, as pointed out by Peierls, and methods of combining them with the other processes have been proposed by Klemens,[5] Ziman,[6] Callaway,[7] and Armstrong.[8] Callaway's procedure, which combines those of Klemens and Ziman, and uses the principle that normal processes do not change the total quasimomentum of the phonon gas, has been favored in the analysis of experimental data, since it yields correctly the known limiting cases of strong N processes, and frequency-independent R processes (resistive processes, the combination of defect scattering, boundary scattering, and U processes).

Using the Callaway analysis, it has been possible to fit the observed thermal conductivities in terms of boundary scattering, point-defect scattering, N processes, and U processes, in a number of cases, notably diamond,[9] lithium fluoride,[10,11] and sodium fluoride.[12] The case of lithium fluoride was particularly instructive, since it was possible to change the isotopic composition and thus control the point-defect scattering. The fitting procedure was constrained to use the same expression for N processes and U processes for all the samples. The fitting procedure was confirmed by the fact that the required strength of the N processes agreed both with theory[13] and also with observations of ultrasonic attenuation at very high frequencies, albeit at much lower frequencies than that of the thermal phonons.[14]

It is thus significant that the exponent Θ' thus obtained is substantially lower than $\hbar\omega_z/k$, where ω_z is the lowest zone-boundary frequency. At that time the experimental values of ω_z were not yet available, but now that phonon-dispersion curves for many dielectric crystals have been obtained, there is a clear discrepancy, as can be seen in Table I.

It has been pointed out by one of us[15] that the simultaneous requirements of frequency conservation and the

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TABLE I. Umklapp Exponents. Values of θ_{exp} were derived from a fit to experimental data of the form $W_u \propto \exp(-\theta_{\mathrm{exp}}/T)$; $k\theta_z = \hbar\omega_z$, where ω_z is the lowest zone-boundary frequency.

Crystal	θ_{exp} (K)	θ_z (K)
LiF	170	350
NaF	140	210
NaF (with point defects)	98	210
KCl (with point defects)	40	95
Si	225	350
Ge	132	90
Diamond	300–900	1,200

wave-vector selection rule cannot be satisfied in a three-phonon interaction linking a low-frequency mode with two modes in the vicinity of the zone boundary. Only a mode of some minimum frequency ω_i can undergo a U process; the two high-frequency modes then lie on different polarization branches, and ω_i, a mode of intermediate frequency, is approximately the difference in frequency of these two branches. The transfer of phonon momentum from the thermal modes then proceeds in two steps. The first step is an N process linking the thermal mode to modes of frequency ω_i or higher. The second step is a U process linking those intermediate-frequency modes to the zone-boundary modes. In parallel to that second step, the intermediate modes can also be scattered by point defects, a process which is much stronger at intermediate frequencies than at thermal frequencies (see Fig. 1).

If that point-defect scattering is strong enough, the apparent exponent θ' will be equal to $\hbar\omega_i/k$. In very pure crystals, θ' should be equal to $\hbar\omega_z'/k$, where $\omega_z' = \omega_z + \omega_i$ is the second-lowest zone-boundary frequency. In between those two extremes, the thermal conductivity should be very sensitive to small amounts of point defects.

This paper aims to develop this idea in as quantitative a manner as possible, considering both the complexity of the problem and the uncertainty of the anharmonic parameters needed. One factor which is no longer uncertain are the phonon-dispersion curves, which are now available for many crystals,[16] and which are considered in the present treatment.

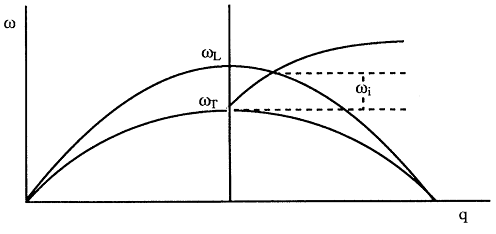

FIG. 1. Schematic representation of dispersion. Here ω_T, ω_L are the transverse and longitudinal frequency at the zone boundary, respectively. ω_i is the lowest frequency that can undergo a U process in the direction.

II. TWO-STEP PROCESS

A. General scheme

Let us consider an N process which links a low-frequency mode to high-frequency modes near the zone boundary. The selection rules (in an extended zone) are

$$\mathbf{q}+\mathbf{q}'=\mathbf{q}'' , \tag{1}$$

$$\omega+\omega'=\omega'' . \tag{2}$$

When $\omega \ll \omega' \sim \omega''$, the q' mode and q'' mode must belong to the same polarization branch. Since $q \ll q' \sim q''$ and from the selection rules (1) and (2) become

$$\omega = \left| \frac{\partial \omega'}{\partial q'} \right| \cdot \mathbf{q} = v_g' \cdot \mathbf{q} \le |v_g'||\mathbf{q}| , \tag{3}$$

where v_g' is the group velocity of q' mode. Since $\omega = v_p q$, where v_p is the phase velocity of q mode, the selection rules are satisfied only if $v_p \le v_g'$. But v_g' is very small near the zone boundary because of dispersion, therefore the direct interactions between low-frequency modes and zone-boundary modes are forbidden. Thus the momentum transfer from low-frequency modes cannot proceed directly but in two steps. The first step is an N process which can transfer momentum from the low-frequency modes to those higher-frequency modes or modes of intermediate frequency which can interact with zone-boundary modes directly; the second step is then an allowed U processes.

If we assume that phonons reside mostly in the transverse branch at very low temperatures, the N process which satisfies the condition $\omega \ll \omega' \sim \omega''$ is a process of the type $T+L \leftrightarrow L$, where T, L represent modes of transverse and longitudinal polarization. The U process in the second step is a process of the type $L+T \leftrightarrow L$ or $L+T \leftrightarrow O$, where the first longitudinal mode is the intermediate-frequency mode and O represents the optical mode.

The first step is an N process and has a total relaxation rate calculated by a Landau-Rumer process,[17] i.e.,

$$\frac{1}{\tau_{\mathrm{LR}}} \propto \omega T^4 C , \tag{4}$$

where $C = \int_0^\infty x^4 \exp(x)/[\exp(x)-1]^2 dx$. The relaxation rate of those N processes which connect low-frequency phonons to intermediate-frequency range $\omega_1 \le \omega \le \omega_j$ is only a fraction, namely,

$$\frac{1}{\tau_N} = \frac{C_{ij}}{C} \frac{1}{\tau_{\mathrm{LR}}} , \tag{5}$$

where

$$C_{ij} = \int_{x_i}^{x_j} \frac{x^4 \exp(x)}{[\exp(x)-1]^2} dx , \quad x_i = \frac{\hbar\omega_i}{kT} , \quad x_j = \frac{\hbar\omega_j}{kT} .$$

B. Total relaxation time of two-step process

Let us consider two frequency reservoirs, one is the thermal frequency (ω) reservoir and the other is the intermediate-frequency (ω_i) reservoir. Let the relaxation rate for the N process from the thermal reservoir to the intermediate reservoir from the point of view of the thermal-frequency mode be $1/\tau_N$, the relaxation rate for the N process from the intermediate reservoir to the thermal reservoir from the point of view of the intermediate-frequency mode be $1/\tau'_N$, and the relaxation rate of the resistive or R process for the intermediate frequency be $1/\tau_R$. Under the action of the N processes alone, the displaced phonon distribution is given by

$$N=\frac{1}{\exp(\hbar\omega-\boldsymbol{\lambda}\cdot\mathbf{q})/kT-1}\ , \tag{6}$$

where $\boldsymbol{\lambda}/\hbar$ is a velocity parameter, the drift velocity in the direction of heat flow. In a quasiequilibrium state, there should be no net momentum exchange between the thermal reservoir and the intermediate reservoir, so that

$$\left|\left(\frac{dP}{d\lambda}\right)\frac{\lambda-\lambda_i}{\tau_N}\right|=\left|\left(\frac{dP}{d\lambda}\right)_i\frac{\lambda_i-\lambda}{\tau'_N}\right|\ , \tag{7}$$

where λ_i is the anisotropy parameter of the intermediate reservoir. One can find that $(dP/d\lambda)$ is proportional to heat capacity C due to thermal modes and $(dP/d\lambda)_i$ is proportional to C_i, the heat capacity due to those modes only whose frequency is above ω_i. From Eq. (7),

$$\frac{\tau_N}{\tau'_N}\approx\frac{C}{C_i}\ . \tag{8}$$

In steady state with a temperature gradient, the momentum rate which the intermediate reservoir receives from the thermal reservoir is equal to the rate at which the intermediate reservoir loses momentum by resistive processes, i.e.,

$$\frac{\lambda-\lambda_i}{\tau'_N}=\frac{\lambda_i}{\tau_R}\ . \tag{9}$$

Equating the rate of loss of momentum of thermal modes to the rate of transfer of momentum to the intermediate reservoir,

$$\frac{\lambda}{\tau}=\frac{\lambda-\lambda_i}{\tau_N}\ . \tag{10}$$

From Eqs. (8), (9), and (10), we find the expression of the effective total relaxation time τ of the thermal modes to be

$$\tau(\omega)=\tau_N(\omega)+\frac{C}{C_i}\tau_R(\omega_i)\ , \tag{11}$$

where τ_N is given by Eq. (5). If the intermediate-frequency reservoir has a range between ω_i and ω_j, Eq. (11) becomes

$$\tau(\omega)=\frac{C}{C_{ij}}[\tau_{\mathrm{LR}}(\omega)+\tau_R(\omega_i)]\ , \tag{12}$$

and if the upper limit of the intermediate reservoir is high enough, C_{ij} is replaced by C_i.

III. ESTIMATION OF THE UMKLAPP PROCESS RATE

The Umklapp process is the intrinsic thermal resistive process in a crystal. This momentum-nonconserving process cannot occur in a continuum, but only in discrete lattice structure. Its most important effect is always to "flip over" the component of energy flux parallel to the relevant reciprocal-lattice vector and thus contributes to thermal resistance. In a reduced zone picture

$$\mathbf{q}+\mathbf{q}'=\mathbf{q}''+\mathbf{b}\ . \tag{13}$$

In reciprocal space, the first Brillouin zone is the irreducible representation zone for all quasimomentum vector $\mathbf{q}$. The boundaries of that primitive cell are the perpendicular bisectors of the shortest reciprocal-lattice vector $\mathbf{b}$'s. In the case of the fcc crystals which are considered in this paper, there are 14 such principal reciprocal-lattice vectors or directions. We evaluate the relaxation rate for a thermal phonon $\mathbf{q}$ parallel to a principal direction.

At low temperatures the important U process is the combining process (13) where q is small, because the major contribution to thermal conduction comes from low-frequency thermal phonons. The interacting modes $\mathbf{q}'$ and $\mathbf{q}''$ are high-frequency modes near the zone boundary. The single-mode relaxation rate of a thermal or intermediate-frequency mode $\mathbf{q}$, defined as the rate when only mode $\mathbf{q}$ departs from equilibrium, can be written as[18]

$$\frac{1}{\tau_U}=\sum_{\mathbf{q}'}2|C_3|^2\frac{\hbar}{M^3\omega\omega'\omega''}\pi\delta_t(\omega+\omega'-\omega'')(N'_0-N''_0)\ , \tag{14}$$

where $|C_3|^2=(4\gamma^2/3G)(M^2/v^2)\omega^2\omega'^2\omega''^2$, γ is the Grüneisen parameter, G is the number of atoms per unit volume, v is the sound velocity, M is the atomic mass,

$$\pi\delta_t(\omega+\omega'-\omega'')=\frac{d}{dt}\left[\frac{1-\cos\Delta\omega t}{\Delta\omega^2}\right]\ ,$$

and N'_0,N''_0 are the equilibrium occupation of mode q',q'', respectively. Now $N'_0-N''_0\approx\exp(-x')$, since $\exp(-x')\gg\exp(-x'')$ and the summation can be replaced by integration as $\sum_{q'j}\approx\eta[Ga^3/(2\pi)^3]\int dq'$, where η represents the number of polarizations of the interacting mode q'. Thus Eq. (14) becomes

$$\frac{1}{\tau_U}\approx\eta\frac{\gamma^2\hbar}{3\pi^2\rho v^2}\int_{\mathbf{q}'}dS'\int\frac{d\Delta\omega}{v_g}\omega\omega'\omega''\delta_t(\Delta\omega)\exp(-x')\ , \tag{15}$$

where ρ is density of crystal, $\Delta\omega=\omega+\omega'-\omega''$, $v_g=|\partial\Delta\omega/\partial q'|_n$ is the group velocity perpendicular to surface S' which is the locus of $\mathbf{q}'$ satisfying the restriction $\Delta\omega=0$, and $x'=\hbar\omega'/kT$. To evaluate the single-mode relaxation rate of mode $\mathbf{q}$, one integrates over all possible $\mathbf{q}'$ modes. But to integrate through the surface S' one must consider dispersion at the zone boundary. Considering the actual dispersion relation, the conservation of energy $\omega+\omega'=\omega''$ and the quasimomentum selection rule $\mathbf{q}+\mathbf{q}'=\mathbf{q}''+\mathbf{b}$, several types of U processes are possible, such as $T+T\leftrightarrow L$, $L+T\leftrightarrow L$, $T+T\leftrightarrow 0$, and $L+T\leftrightarrow 0$. Their relative importance will be discussed in Sec. IV. To evaluate a relaxation rate, we proceed by the following scheme: (1) The thermal mode $\mathbf{q}$ is taken parallel to a reciprocal-lattice vector $\mathbf{b}$ and only this reciprocal-lattice vector is considered, so that energy conservation is satisfied approximately in the vicinity of the corresponding zone boundary. (2) The known dispersion curves in degeneracy directions $\langle 1,0,0\rangle$'s and $\langle 1,1,1\rangle$'s of the fcc crystals are considered here, and are approximated by sine curves in case of transverse and longitudinal branches and by straight lines in case of optical branches. In each degenerate direction, one can find a frequency range ω_i to ω_j of the modes which can undergo a U process directly. (3) The strength of the U processes is uniform for all modes in this frequency range.

We now estimate the relaxation rate of the type $L+T\leftrightarrow L$ for a longitudinal mode of frequency ω_i and wave vector $\mathbf{q}_i$ parallel to the reciprocal-lattice vector $\mathbf{b}$ and thus of magnitude $b/4\pi\sin^{-1}(\omega_i/\omega_L)$ where $|\mathbf{b}|=4\pi/a$ for $\langle 1,0,0\rangle$ and $2\sqrt{3}\pi/a$ for $\langle 1,1,1\rangle$, and ω_L is longitudinal zone-boundary frequency. We assume frequencies $\omega'\approx\omega_T$ and $\omega''\approx\omega_i+\omega_T$ on the integral surface S', where ω_T is the transverse zone-boundary frequency. Thus

$$\frac{1}{\tau_u}\approx\eta\frac{\gamma^2\hbar}{3\pi^2\rho v^2 v_g}\omega_i\omega_T(\omega_i+\omega_T)\exp(-\hbar\omega_T/kT)\int_{q'}dS' \ . \tag{16}$$

The problem is to determine the magnitude of the surface $\int dS'$. The integral surface must be near the first Brillouin-zone boundary, thus one approximates the integral surface S' by the plane zone boundary which is perpendicular to reciprocal-lattice vector $\mathbf{b}$. Let $\int dS'=\pi r_c^2$. The effective radius r_c from center of the zone boundary is chosen so that the interacting mode $\mathbf{q}'$ on the integral surface satisfy the momentum condition (13) with the unique reciprocal-lattice vector. Using the geometric diagram of Fig. 2, one can get the optimum value of r_c as

$$r_c=R\left|\frac{b}{2}-q_i\right|\Big/\left|\frac{b}{2}\right| \ , \tag{17}$$

where R is the radius of a circle inscribed in the zone-boundary area, i.e., $R=\pi/(\sqrt{2}a)$ for $\langle 1,0,0\rangle$ direction and $(\sqrt{3}\pi)/(\sqrt{2}a)$ for $\langle 1,1,1\rangle$ direction. Finally, the expression of the relaxation rate of the U process of the type $L+T\leftrightarrow L$ becomes

$$\frac{1}{\tau_U}\approx\frac{2\gamma^2\hbar}{3\pi\rho v^2 v_g}\omega_i\omega_T(\omega_i+\omega_T)r_c^2\exp(-\hbar\omega_T/kT) \ , \tag{18}$$

where v is the sound velocity of the thermal mode and $v_g=|\partial\omega''/\partial q''|$ at $\omega''=\omega_i+\omega_T$ in the direction of the reciprocal-lattice vector $\mathbf{b}$, i.e., perpendicular to integral surface S'. While r_c could be used as an adjustable parameter, in the present treatment it is fixed by Eq. (17).

The expression for processes of the type $T+T\leftrightarrow L$ is the same as Eq. (18). The expression for processes of the type $T+L\leftrightarrow L$, which are important U processes in the case of silicon and germanium, is given as

$$\frac{1}{\tau_U}\approx\frac{\gamma^2\hbar}{3\pi\rho v^2 v_g}\omega_i(\omega_L-\omega_i)\omega_L r_c^2\exp[-\hbar(\omega_L-\omega_i)/kT] \ , \tag{19}$$

where $v_g=|\partial\omega'/\partial q'|_n$ at $\omega'=\omega_L-\omega_i$. The expressions for processes of the type $T+L\leftrightarrow 0, T+T\leftrightarrow 0$ are basically the same as the above, but with a reduction parameter μ and some uncertainty in the value of $v_g=|\partial\Delta\omega/\partial q'|$. This will be discussed in Sec. V.

IV. APPLICATION OF TWO-STEP THEORY

A. Two frequency ranges

If the only resistive processes were U processes, one would divide the frequency range at ω_i, the threshold frequency at which a phonon can undergo a U process. A phonon $\omega<\omega_i$ then reaches equilibrium by two steps: an N process transferring momentum to frequencies above ω_i (or just above ω_i, since the heat capacity drops rapidly with frequency) followed by a U process. However, in many crystals the scattering by point defects is strong enough to be more important than U processes near ω_i. The second step is then point-defect scattering, and can also be important below ω_i. One needs a criterion dividing the frequency range into $\omega>\omega_R$, where the second

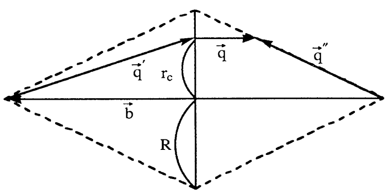

FIG. 2. Geometrical diagram to determine the integral surface at the zone boundary. Here r_c is the optimum radius of the integral surface in the process $\mathbf{q}+\mathbf{q}'=\mathbf{q}''+\mathbf{b}$, where $\mathbf{q}$ is thermal mode parallel to the principal direction.

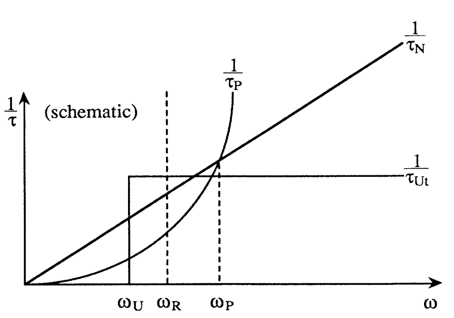

FIG. 3. Schematic representation of relaxation rates as function of frequency in case of $\omega_R<\omega_P$. Here $1/\tau_P$ is point-defect scattering, $1/\tau_N$ is the N process, $1/\tau_{Ut}$ is the U process of the transverse mode, and ω_U is the onset frequency of the U process.

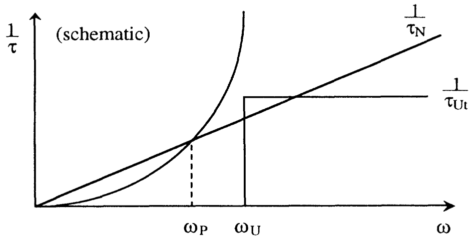

FIG. 4. Schematic representation of relaxation rates as function of frequency in the case of $\omega_R = \omega_P$.

step (R processes, combining U processes and point-defect scattering) is significant and $\omega < \omega_R$, where momentum is transferred mainly by N processes into that upper frequency range.

We divide the thermal phonons into two such groups by using the following:

$$\frac{1}{\tau_N}(\omega_R) = \frac{1}{\tau_R}(\omega_R) , \tag{20}$$

where $1/\tau_N$ is the relaxation rate of the normal process and $1/\tau_R$ can be all other resistive process. In the first group N processes are stronger than R processes and in the second group R processes are stronger.

Let ω_P be the frequency at which the relaxation rate of the N process is equal to that of point-defect scattering, that is

$$\frac{1}{\tau_N}(\omega_P) = \frac{1}{\tau_P}(\omega_P) . \tag{21}$$

We assume that most low-temperature thermal phonons are transverse mode. Thus we consider only transverse U processes and point-defect scattering as important direct resistive processes (R process), and transverse phonon N processes, as discussed by Landau and Rumer, as the important N processes. Equation (20) becomes

$$\frac{1}{\tau_{\mathrm{LR}}} = \frac{1}{\tau_{Ut}} + \frac{1}{\tau_P} , \tag{22}$$

where $1/\tau_{Ut}$ represents the relaxation rate of the U process of the type $T+T \leftrightarrow L,0$ and $T+L \leftrightarrow L,0$, where the first branch is the thermal mode. The frequency ω_R changes as temperature changes, since $1/\tau_{\mathrm{LR}} \propto T^4$ and $1/\tau_{Ut} \propto \exp(-1/T)$. Two typical cases are shown schematically in Figs. 3 and 4.

B. Classification of second steps

In the two-step process, we consider only point-defect scattering and the U process in the second-step process and follow the simplification described below.

We classify the second step as follows. The frequency ω_R is never greater than ω_P, hence it is convenient to consider two different cases: (i) $\omega_P < \omega_i$ (Fig. 3) and (ii) $\omega_P \geq \omega_i$ (Fig. 4), where ω_i is the lowest frequency which can undergo a longitudinal U process of the type $L+T \leftrightarrow (L$ or 0).

In case of (i), i.e., $\omega_P < \omega_i$, we have three kinds of second-step processes for the three frequency ranges A, B, and C:

(A) In the frequency range from ω_P to ω_i only point-defect scattering is considered, approximated by a constant relaxation rate $1/\tau_P(\omega_P)$.

(B) In the frequency range ω_i to ω_j, U processes can occur; hence point-defect scattering and U processes are considered in this range, approximated by a constant relaxation rate $(1/\tau_P)(\omega_i)+(1/\tau_{U1})(\omega_i)$, where $1/\tau_{U1}$ represents longitudinal U process of the type $L+T \leftrightarrow (L$ or 0).

(C) In the frequency above ω_j, only point-defect scattering can occur, with a constant relaxation rate $(1/\tau_P)(\omega_j)$.

In the case of (ii), i.e., $\omega_P \geq \omega_i$, point-defect scattering is neglected in the range $\omega < \omega_i$ because it is quite weak compared to N processes. In the range above ω_i both U processes and point-defect scattering are considered (range B) and above ω_j (range C) only point-defect scattering occurs.

Thus the relaxation time of two-step processes for each frequency ranges are given as follows: Range (A);

$$\tau(\omega) = \frac{C}{C_{Pi}}[\tau_{\mathrm{LR}}(\omega) + \tau_P(\omega_P)] , \tag{23}$$

where $\omega < \omega_R$. Range (B);

$$\tau(\omega) = \frac{C}{C_{ij}}[\tau_{\mathrm{LR}}(\omega) + \tau_R(\omega_i)] , \tag{24}$$

where

$$\frac{1}{\tau_R}(\omega_i) = \frac{1}{\tau_{U1}}(\omega_i) + \frac{1}{\tau_P}(\omega_i) ,$$

provided $\omega < \omega_R$ if $\omega_R < \omega_i$ or $\omega < \omega_i$ if $\omega_R > \omega_i$. Range (C);

$$\tau(\omega) = \frac{C}{C_i}[\tau_{\mathrm{LR}}(\omega) + \tau(\omega_j)] . \tag{25}$$

Here C denotes the total specific-heat integral, C_i is the part above ω_i, and C_{Pi} and C_{ij} are the parts between ω_P and ω_j, respectively.

C. Use of isotropic continuum approximation

In the isotropic continuum approximation, the integral surface of q space is the surface of a cone of which half angle is generally $\cos^{-1}(v_T/v_L) \approx 48.2°$ because of $v_T/v_L \sim 2/3$ for the most crystals. We want to use the isotropic continuum as an approximation to the fcc structure for the first-step process (Landau-Rumer process). The angle between $\langle 1,0,0 \rangle$ and $\langle 1,1,1 \rangle$ is 54.7°. Since we choose the 14 principle directions for thermal phonons, the majority of phonon in the $\langle 1,0,0 \rangle$ directions are scattered into $\langle 1,1,1 \rangle$ directions and the majority of phonon of $\langle 1,1,1 \rangle$ directions are scattered into $\langle 1,0,0 \rangle$ directions by the N process (Landau-Rumer process) in the approximation. Thus we have two different values for ω_R for each direction of $\langle 1,0,0\rangle$'s and $\langle 1,1,1\rangle$'s, to be called $\omega_{R\langle 1,0,0\rangle}$ and $\omega_{R\langle 1,1,1\rangle}$. The $\omega_{R\langle 1,0,0\rangle}$ is determined by the equation $1/\tau_{\mathrm{LR}}=1/\tau_{Ut\langle 1,0,0\rangle}+1/\tau_P$ and the $\omega_{R\langle 1,1,1\rangle}$ is determined by the equation $1/\tau_{\mathrm{LR}}=1/\tau_{Ut\langle 1,1,1\rangle}+1/\tau_P$, where $1/\tau_{Ut\langle 1,0,0\rangle}$, $1/\tau_{Ut\langle 1,1,1\rangle}$ refer to transverse U processes for the directions of $\langle 1,0,0\rangle$, $\langle 1,1,1\rangle$, respectively. Thus the total relaxation time of the two-step process is divided into two different relaxation times as, for example, for frequency range B,

$$\tau_{2\langle 1,0,0\rangle}=\frac{C}{C_{ij}}[\tau_{\mathrm{LR}}+\tau_{R\langle 1,1,1\rangle}]$$

for the thermal phonon of the $\langle 1,0,0\rangle$ direction and

$$\tau_{2\langle 1,1,1\rangle}=\frac{C}{C_{ij}}[\tau_{\mathrm{LR}}+\tau_{R\langle 1,0,0\rangle}]\ ,$$

where

$$\frac{1}{\tau_{R\langle 1,0,0\rangle}}=\frac{1}{\tau_{U1\langle 1,0,0\rangle}}(\omega_i)+\frac{1}{\tau_P}(\omega_i)$$

and

$$\frac{1}{\tau_{R\langle 1,1,1\rangle}}=\frac{1}{\tau_{U1\langle 1,1,1\rangle}}(\omega_i)+\frac{1}{\tau_P}(\omega_i)\ .$$

V. APPLICATIONS

We use the Callaway's expression[7] to calculate thermal conductivity. Callaway's expression for thermal conductivity can be written

$$K=K_1+K_2\ , \tag{26}$$

where

$$K_1=\frac{k}{2\pi^2 v}\left[\frac{k}{\hbar}\right]^3 T^3\int_0^{\Theta/T}\frac{\tau_c x^4\exp(x)}{[\exp(x)-1]^2}dx \tag{27}$$

and

$$K_2=\frac{k}{2\pi^2 v}\left[\frac{k}{\hbar}\right]^3 T^3\frac{\left[\int_0^{\Theta/T}(\tau_c/\tau_N)\{x^4\exp(x)/[\exp(x)-1]^2\}dx\right]^2}{\int_0^{\Theta/T}(\tau_c/\tau_N\tau_R)\{x^4\exp(x)/[\exp(x)-1]^2\}dx}\ . \tag{28}$$

The combined relaxation time τ_c is defined by $1/\tau_c=1/\tau_R+1/\tau_N$. Now, the N process $T+L\leftrightarrow L$ is considered an important normal process at low temperatures. Thus $1/\tau_N=1/\tau_{\mathrm{LR}}$. The relaxation rate of resistive process is

$$\frac{1}{\tau_R}=\frac{1}{\tau_2}+\frac{1}{\tau_{Ut}}+\frac{1}{\tau_P}+\frac{1}{\tau_B}+\frac{1}{\tau_{\mathrm{op}}}\ ,$$

where $1/\tau_2$ is the relaxation rate of the two-step process, which is taken as the mean value for the 14 principal directions, i.e.,

$$\frac{1}{\tau_2}=\frac{1}{14}\left[\frac{6}{\tau_{2\langle 1,0,0\rangle}}+\frac{8}{\tau_{2\langle 1,1,1\rangle}}\right]\ .$$

Here we consider the two-step processes as pure resistive processes though they contain an N process in the first step. In the first step, N processes are very restricted for the specially chosen frequency range, i.e., $\omega<\omega_R$, and ω_R is proportional to temperature. Thus at low temperatures, we neglect the double counting of N processes. Also $1/\tau_{Ut}$ is the relaxation rate of the U process for transverse modes of thermal phonons, taking the mean value as

$$\frac{1}{\tau_{Ut}}=\frac{1}{14}\left[\frac{6}{\tau_{Ut\langle 1,0,0\rangle}}+\frac{8}{\tau_{Ut\langle 1,1,1\rangle}}\right]\ ,$$

$1/\tau_P$ is the point-defect scattering, and $1/\tau_B$ is the boundary scattering; scattering by dislocations has been disregarded. Also $1/\tau_{\mathrm{op}}$ is the interaction with the optical mode (see the Appendix). In the interaction with the optical mode of the $T+T\leftrightarrow 0$ or $L+T\leftrightarrow 0$ processes, an adjustable reduction parameter μ is used. We choose $\mu=\frac{1}{2}$ from the average polarization factor between the acoustic mode and the optical mode in a one-dimensional crystal. We also need to know the value of the group velocity of the optical mode. We replace it by an average value,

$$v_g=\left|\frac{\omega_{\mathrm{op}}(0)-\omega_{\mathrm{op}}(q_z)}{q_z}\right|\ .$$

Where the values of $\omega_{\mathrm{op}}(0)$ and $\omega_{\mathrm{op}}(q_z)$ are uncertain, we choose values within experimental limits which give the best fit. Generally the contribution of the interaction with the optical mode is not strong.

The sound velocity v is determined by taking the harmonic average of transverse and longitudinal modes in

TABLE II. Parameters used in the calculations as adjustable constants: Grüneisen γ with thermal-expansion values in parenthesis; point-defect scattering parameter α, derived from a fit at low temperatures, with isotope values in parenthesis; L smallest external dimension.

	θ (K)	γ	α (sec$^{-1}K^4$)	L (cm)
99.99% ^{7}LiF			0.021(0.0005)	1.10
97.2% ^{7}LiF	583	1.4 (1.5)	0.126(0.126)	0.75
92.6% ^{7}LiF			0.318(0.318)	0.66
NaF	392	1.55(1.5)	0.20(0.08)	0.58
Diamond	1778	0.52(0.9)	0.031(0.004)	0.165
Si	512	0.56(0.56)	0.5(0.47)	0.25
Ge	297	0.76(0.76)	0.7(0.45)	0.25

TABLE III. The types of U processes used in the calculations in the frequency ranges, indicated in units of 10^{13} rad/sec.

	Type of process	⟨100⟩ direction	⟨111⟩ direction
LiF	$L+T=L$	1.57–1.98	2.83–4.06
	$T+T=L$	1.45–2.39	2.17–3.90
	$L+T=0$	The same as $L+T=L$	Neglected
	$T+T=0$	The same as $T+T=L$	1.80–3.90
NaF	$L+T=L$	1.86–2.64	2.02–2.84
	$T+T=L$	1.46–2.76	1.64–3.30
	$L+T=0$	The same as $L+T=L$	Neglected
	$T+T=0$	The same as $T+T=L$	Neglected
Diamond	$L+T=L$	6.22–8.15	7.57–10.9
	$T+T=L$	5.56–15.2	5.79–10.4
Si	$L+T=L$	3.96–6.06	3.52–5.42
	$T+T=L$	2.18–2.83	1.75–2.16
	$T+L=L$	1.80–2.83	1.75–2.16
Ge	$L+T=L$	2.36–6.32	2.30–3.55
	$T+T=L$	1.21–1.51	1.01–1.19
	$T+L=L$	0.91–1.51	0.63–1.19

the principal directions of ⟨1,0,0⟩, ⟨1,1,0⟩, and ⟨1,1,1⟩ as $1/v=1/3(2/v_T+1/v_L)$ and where the transverse velocity v_T and the longitudinal velocity v_L are given by the following average over directions:

$$v_T=\frac{6v_{T\langle 1,0,0\rangle}+12v_{1T\langle 1,1,0\rangle}+12v_{2T\langle 1,1,1\rangle}+8v_{T\langle 1,1,1\rangle}}{38}$$

and

$$v_L=\frac{6v_{L\langle 1,0,0\rangle}+12v_{L\langle 1,1,0\rangle}+8v_{L\langle 1,1,1\rangle}}{26}\ .$$

To determine the sound velocity of each mode, we use data of elastic constants.[19–22]

The calculations are compared with existing data of LiF, NaF, diamond II-a, Si, and enriched ^{74}Ge. These materials were chosen because thermal-conductivity mea-

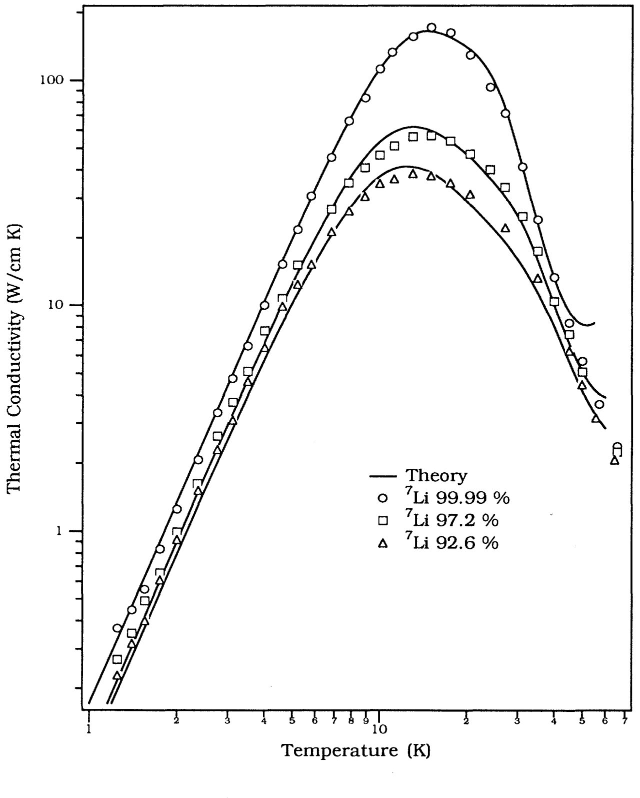

FIG. 5. Thermal conductivity of LiF.

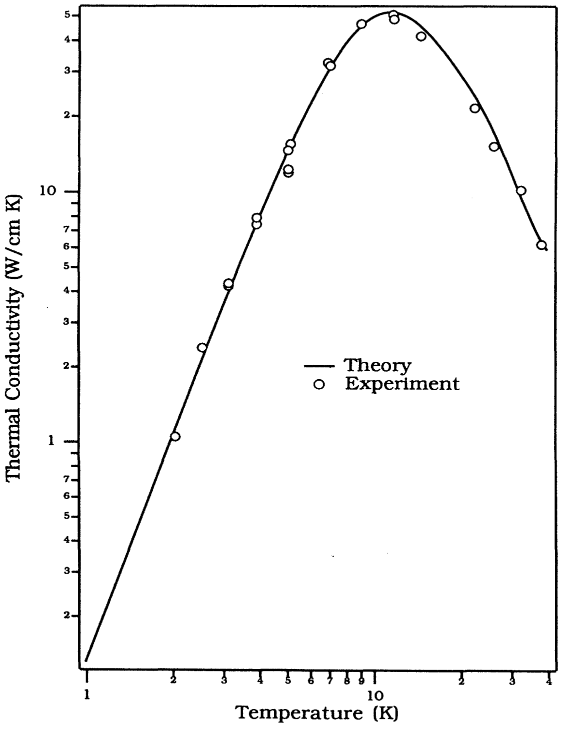

FIG. 6. Thermal conductivity of NaF.

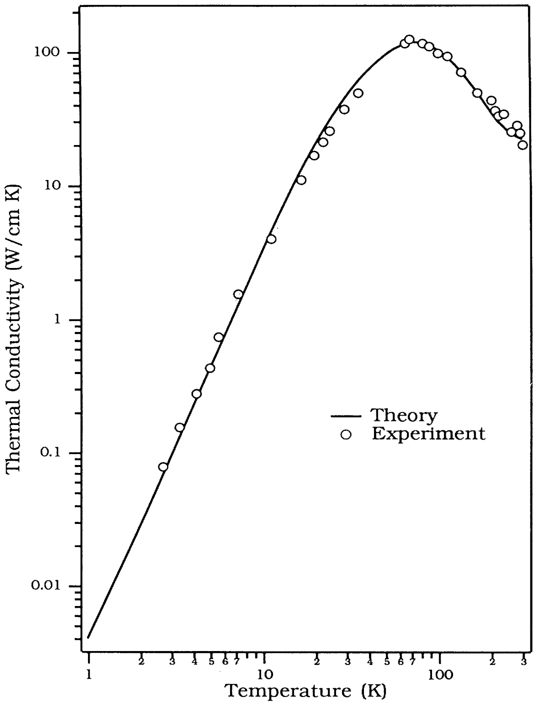

FIG. 7. Thermal conductivity of diamond.

surements have been made on good crystals. In order to fit the existing thermal-conductivity data, we use the Grüneisen parameter γ, the point-defect scattering strength α, and the smallest dimension of the crystal as adjustable parameters. The experimental and theoretical values of Grüneisen parameter and Debye temperature are from Ref. (4), where the Debye temperatures are taken for acoustic branches only. The characteristic parameters are given in Table II.

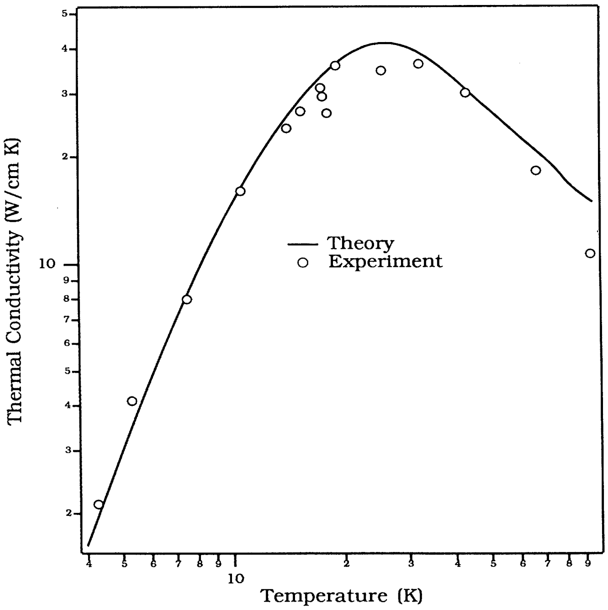

FIG. 8. Thermal conductivity of Si.

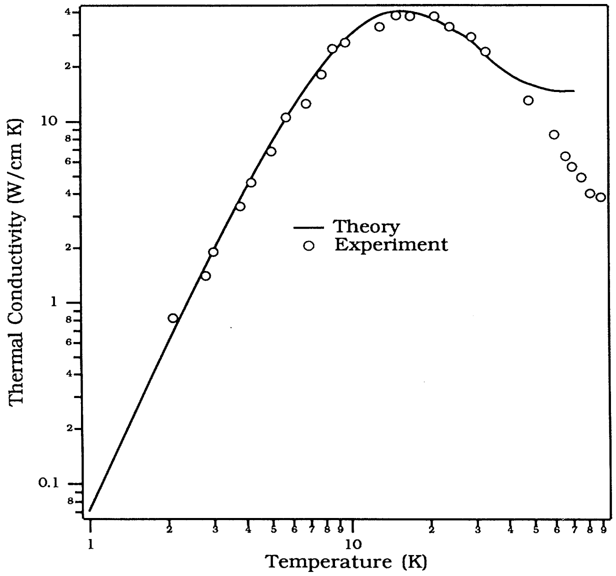

FIG. 9. Thermal conductivity of Ge.

(i) LiF: We are comparing calculations with the experimental data of Thacher[11] for 99.99%, 97.2%, and 92.6% isotope ^{7}Li as shown in Fig. 5. The most important U processes that are considered are shown in Table III.

(ii) NaF: The calculations are compared with the experimental data of Taylor, Albers, and Pohl[12] (Fig. 6). The value of point-defect scattering in parenthesis is for the effective extra point defect to fit pure crystal data used by Walker.[23]

(iii) Diamond: The type II-2 is one of the purest nonconducting diamonds which has the highest thermal conductivity. Thus our calculation is compared with the data of diamond II-a. The calculation is compared with the data of Berman, Foster, and Ziman[9] as shown in Fig. 7.

(iv) Si and enriched ^{74}Ge: These crystals are insulators and there are no carriers to scatter phonons. In the case of Si and Ge, the U processes of the type $T+L\leftrightarrow L$ have to be considered as important processes as well as that of the type $T+T\leftrightarrow L$ because the threshold frequency of the U process is lower than that of the type $T+T\leftrightarrow L$. The calculations are compared with the data of Glassbrenner and Slack[24] and Geballe and Hull,[25] respectively, for Si and ^{74}Ge as shown in Figs. 8 and 9.

As the temperature increases, calculations deviate from the experimental data because the N process is cut at the transverse zone-boundary frequency.

VI. CONCLUSION

The present treatment of Umklapp processes clarifies their role in the thermal resistive process. Only modes above some minimum frequency ω_i can interact with modes near the zone boundary. The resistive process is a two-step process. Thermal modes interact by N processes to modes $\omega > \omega_R$, followed by either a U process, by point-defect scattering, or by these processes in combination.

Using a strength of point defects derived from fitting the region below the conductivity maximum, and treating the anharmonicity parameter γ as adjustable, good fits were obtained to experimental thermal-conductivity curves for a number of crystals. The quality of the fits is not in itself remarkable, however, it was not necessary to invoke the exponent in the Umklapp resistance as an adjustable parameter. Instead the shape of the phonon-dispersion curves, which are now known, were used in the calculations.

The thermal conductivity is quite sensitive to point-defect scattering and it is expected that as crystals of higher purity become available, their thermal conductivity in the "Umklapp" regime will be substantially larger.

APPENDIX: RELAXATION RATE OF INTERACTION WITH OPTICAL MODE

In the case of LiF and NaF, the optical dispersion curve intercepts all longitudinal modes in all directions—$\langle 1,0,0\rangle$, $\langle 1,1,0\rangle$, and $\langle 1,1,1\rangle$. Thus a normal process of the type $T+L\leftrightarrow 0$ can be considered as a resistive process because the group velocity of optical mode is so small that the optical mode almost cannot contribute to thermal conduction.

For simplicity, let us assume that optical mode has the same frequency, i.e., the optical branch is completely flat. If the optical-mode frequency is constant in all directions, the selection rules of the process can be written

$$\omega+\omega'=\omega_{\text{op}} , \tag{A1}$$

$$\mathbf{q}+\mathbf{q}'=\mathbf{q}'' , \tag{A2}$$

where ω_{op} is the frequency of optical mode, which is the average value of the maximum and minimum value of the transverse-optical frequency. In nondispersive continuum approximation, (A1) becomes

$$v_T q+v_L q'=\omega_{\text{op}} . \tag{A3}$$

Thus,

$$q'=\frac{\omega_{\text{op}}-\omega}{v_L} . \tag{A4}$$

The single-mode relaxation rate is

$$\frac{1}{\tau_{\text{op}}}=\sum_{q'} 2|\mu C_3|^2\frac{\hbar^3}{M^3\omega\omega'\omega''}\delta_t(\omega+\omega'-\omega'')[N_0'-N_0''] , \tag{A5}$$

where μ is a reduction parameter—here $\mu=\frac{1}{2}$. Since $\omega<\omega'<\omega''$ in the case of LiF and NaF at low temperatures, $N_0'-N_0''\approx\exp(-x_{\text{op}})[\exp(x)-1]$. Thus,

$$\frac{1}{\tau_{\text{op}}}\approx\mu^2\frac{\gamma^2\hbar}{3\pi^2\rho}\frac{1}{v_g v_T^2}\int dS'\int d\Delta\,\omega\delta_t(\Delta\omega)\omega\omega'\omega''\exp \\ \times(-x_{\text{op}})[\exp(x)-1] , \tag{A6}$$

where $v_g=|\partial\Delta\omega/\partial q'|$ at $\omega'=\omega_{\text{op}}-\omega$, thus we take the group velocity as v_L. Now the integral surface in $\mathbf{q}'$ space can be taken as a sphere with radius $(\omega_{\text{op}}-\omega)/v_L$. Then the integration can be reduced as follows:

$$\int dS'\int d\Delta\omega\delta_t(\Delta\omega)\omega\omega'\omega''\exp(-x_{\text{op}})[\exp(x)-1]\approx 4\pi\left[\frac{\omega_{\text{op}}-\omega}{v_L}\right]^2\omega(\omega_{\text{op}}-\omega)\omega_{\text{op}}\exp(-x_{\text{op}})[\exp(x)-1] .$$

Thus the relaxation rate of interaction of the type $T+L\leftrightarrow 0$ can be written as

$$\frac{1}{\tau_{\text{op}}}\approx\frac{\pi\gamma^2\hbar}{3\pi^2\rho}\frac{1}{v_T^2 v_L^4}\omega\omega_{\text{op}}(\omega_{\text{op}}-\omega)^3\exp(-x_{\text{op}})[\exp(x)-1] . \tag{A7}$$

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