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N processes, the relaxation-time approximation, and lattice thermal conductivity

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The two-fluid theory of phonon transport and thermal conductivity recently proposed by the author is refined, with the major source of error identified as the previous neglect of the subset of normal processes called NN processes. A correction is provided for these processes, which are mainly those of phonon splitting. This correction, based on the Callaway approximation, utilizes two shift parameters in the displaced Planck distribution, one for low-frequency modes and one for high-frequency modes. Comparison with experiment is performed on a group of LiF specimens of varying isotopic purity. The results demonstrate that the refined theory explains the behavior of the thermal conductivity across the region of peak value with high accuracy for the purer specimens. The role of the single-mode relaxation-time approximation is clarified as well as the significance of the linearly-frequency-dependent Landau-Rumer transition rate which tends to dominate the thermal-conductivity calculation. As in the earlier treatment, no explicit account of U processes is required. They are included implicitly in the Landau-Rumer rate along with NR processes, which are N processes ending in reservoir modes. The new formulation, dependent only on known transition-rate expressions, appears to provide a framework for systematic approximation to the Peierls-Boltzmann integral equation.

I. INTRODUCTION

In the theory of lattice thermal conductivity, one must distinguish between processes that conserve phonon quasimomentum (normal anharmonic or N processes) and processes that do not (anharmonic umklapp processes and phonon scattering by boundaries and imperfections). The latter are resistive or R processes. It was already pointed out by Peierls[1] that normal processes cannot be disregarded, but that they contributed to thermal resistance by transferring momentum from one group of modes, where R processes are weak, to other modes where R processes are strong. This effect should be particularly important for point-defect scattering, since that scattering probability is strongly frequency dependent.

In spite of a general understanding of the underlying physics of this problem, there has been no completely satisfactory solution. An early attempt by Klemens[2] divides the modes into two groups: low-frequency modes, which are brought by N processes into equilibrium with the high-frequency modes, and the high-frequency modes, whose equilibrium depends only on R processes. However, this division into two groups at an angular frequency ω_R is arbitrarily taken at $\omega_R = k_B T/\hbar$ (k_B, T, and $\hbar$ are the Boltzmann constant, the absolute temperature, and the reduced Planck constant, respectively).

The present author[3] advanced a similar model, again dividing the modes into two groups, but paying detailed attention to the choice of ω_R. The criterion for choosing ω_R at low temperature was that at this frequency the relaxation rate due to anharmonic N processes with modes of final-state phonon frequency above ω_R should equal the relaxation rate of R processes (at higher temperature ω_R is determined by the dispersion of the lattice waves). Not only is this a more realistic criterion, but it was combined with an improved theoretical knowledge of relaxation rates, and used advances in computational techniques.

Another approach, due to Callaway,[4] makes N processes relax towards a quasiequilibrium distribution, i.e., one shifted in momentum space, while R processes tend to restore true equilibrium; the shift of the quasiequilibrium distribution is chosen so that N processes conserve momentum in the aggregate.

The Callaway theory, definitely superior to that of Klemens, has been widely applied, and the majority of measured low-temperature thermal-conductivity curves have since been analyzed in this manner. However, it does have limitations, and the apparent success of the method is partly based on the fact that the strength of N processes is usually not known, but is treated as an adjustable parameter. The most rigid test of the theory consists of application to a series of different isotopic compositions of the same crystal. This has been done for LiF. In the analysis of Berman and Brock[5] based on the Callaway theory, for example, it was necessary to choose a form for the N-process relaxation rate which differed from theory. The other comparably detailed study of the isotope effect in solid helium is complicated by an uncertainty in the strength of the isotope scattering.

A single-parameter shifted distribution as adopted by Callaway is not completely realistic. The high-frequency modes cannot be shifted as much as the low-frequency modes, but should be nearly in equilibrium. The difference in effectiveness between N processes involving a low-frequency phonon and those involving high-frequency phonons, which formed the rationale of Refs. 2 and 3, is not present in the Callaway theory. Yet N processes do conserve momentum, an effect not considered in Refs. 2 and 3.

The purpose of the present paper is to improve the author's earlier theory[3] by including the momentum-conservation criterion of the Callaway theory, while at the same time accommodating the difference between low- and high-frequency N processes by use of different quasiequilibrium shift parameters for each "fluid," or group of modes. To do so, one has to consider not only the effect of N processes on a low-frequency mode, but also the effect on high-frequency modes due to N processes involving two modes of lower frequency, the "phonon splitting" processes.

The author's theory[3] divides modes into a group with a large departure from equilibrium and a "reservoir" group which is practically at equilibrium, either because the group velocity is small or because modes of the group are strongly affected by R processes. The anharmonic processes are thus no longer divided into N and U processes but into processes involving only modes of the lower group (NN processes) and those linking the two groups (NR processes). It thus does not matter whether the final-state mode in an extended zone representation lies on one side of the zone boundary or the other, since its departure from equilibrium will, in either case, be small. All NR processes are thus treated on the same footing.

The present paper not only considers the possibility of a small average shift in momentum space of the reservoir modes, but also recognizes that there are different polarization branches. Thus, over some range of frequencies the longitudinal modes have a large group velocity, while transverse modes are either highly dispersed or have the top of their spectrum below those frequencies. There is consequently an "overlap" region where reservoir and propagating modes coexist.

This new approach is applied to a series of LiF specimens differing only in isotopic constitution. The modifications of the theory are of most importance when the strongly-frequency-dependent point-defect scattering is strong, i.e., near the conductivity maximum. At high temperature the correction is small.

Since the Boltzmann equation is a linear integral equation, one can, in principle, express the solutions as a set of eigenfunctions of the integral operator. A formal, unified theory along these lines has been developed by Guyer and Krumhansl,[6] encompassing not only steady-state heat transport, but also time-dependent problems as well. They were able to identify the Callaway treatment as a first approximation in their general scheme. Unfortunately, it is not clear how higher-order eigenfunctions may be obtained nor how rapidly the theory converges.

For that reason, the present approach may be generally useful in pointing the way to the next approximation beyond the Callaway theory. Alternatively, with the advent of numerical methods such as have been employed in the photon Boltzmann equation,[7] it may provide the framework for an iterative numerical process.

In Sec. II immediately following, a brief review is given of the two-fluid theory.[3] Section III presents the generalization of that theory, introducing the correction for NN processes including phonon splitting. In Sec. IV, the new approach is applied to LiF, and Sec. V concludes the paper. The Appendix is devoted to a discussion of entropy production by N processes based on a simplified crystal spectrum which relates this production to the strength of the frequency dependence of the resistive transition rate.

II. THE TWO-FLUID MODEL

The theory of Ref. 3 divides the normal modes (or the phonon gas) into two groups, the propagating modes and the reservoir modes. The propagating modes contain the momentum of the phonon gas in a temperature gradient, and the reservoir modes, which are close to equilibrium, act as a momentum sink in the anharmonic processes between these two groups.

The departure of the phonon occupation number from thermal equilibrium can be written in the following form:[4,8]

$$N_q - N_0 = \Phi(\mathbf{q})[\partial N_q/\partial(\hbar\omega)] \tag{1}$$

and

$$\Phi(\mathbf{q}) = -\hbar\omega\alpha(\omega)\mathbf{c}_q\cdot\nabla T/T \ , \tag{2}$$

where $\mathbf{q}$ is the wave vector of a mode, ω its angular frequency, $\mathbf{c}_q$ its group velocity, ∇T the temperature gradient, and $\alpha(\omega)$, a parameter of the dimension of time, is the effective relaxation time which formally describes the solution of the Boltzmann equation.

The rate of change of the distribution function due to anharmonic processes can be written in the form[8]

$$\left.\frac{\partial N_q}{\partial t}\right|_{\mathrm{AN}} \simeq \int [\Phi(\mathbf{q})+\Phi(\mathbf{q}')-\Phi(\mathbf{q}'')]P(\mathbf{q},\mathbf{q}';\mathbf{q}'')d^3q' \ , \tag{3}$$

where $\mathbf{q}''=\mathbf{q}+\mathbf{q}'$, the integration is over all values of $\mathbf{q}'$, but P is nonvanishing only if $\omega+\omega'=\omega''$. Quasiequilibrium occurs, i.e., the integrand vanishes everywhere, if $\mathbf{c}_q\alpha(\omega)$ is the same for all modes. Another case of interest is when $\Phi(\mathbf{q}')$ and $\Phi(\mathbf{q}'')$ are both much smaller than $\Phi(\mathbf{q})$, so that

$$\left.\frac{\partial N_q}{\partial t}\right|_{\mathrm{AN}} \simeq \int \Phi(\mathbf{q})P(\mathbf{q},\mathbf{q}';\mathbf{q}'')d^3q' \ . \tag{4}$$

The relaxation rate thus calculated equated to $(N_q - N_0)/\tau$ defines the "single-mode relaxation time" τ.

At high temperatures, the reservoir modes are the highly dispersive, high-frequency modes for which Φ is small because the group velocity is small [because of Eq. (2) and because elastic scattering processes are then strongest]. At low temperatures extrinsic scattering becomes important. It increases strongly with frequency, makes $\alpha(\omega)$ small for high-frequency modes, and extends the reservoir boundary ω_R to lower frequencies. The propagating modes undergo anharmonic interactions with modes in their own group (NN processes neglected in Ref. 3), and also interact anharmonically with reservoir modes (NR processes).

At low temperatures ω_R is determined by the condition

$$\tau_{NR}(\omega_R) = \tau_I(\omega_R) \ , \tag{5}$$

where τ_I is the relaxation time due to non-momentumconserving processes and τ_{NR} is the relaxation time due to anharmonic processes linking the propagating group and the reservoir group.

Since ω_R thus determined increases with temperature, at sufficiently high temperature ω_R is taken to be ω_{RU}, the threshold frequency for U processes, and approximately the highest frequency of the lowest transverse acoustic branch. As a further approximation, ω_R at low temperature was taken to be proportional to T, as it was found that Eq. (5) did not depart significantly from this proportionality. The constant ratio $x_R = \hbar\omega_R / k_B T$ was taken as an adjustable parameter when fitting thermal-conductivity curves.

The present treatment dispenses with the need to choose x_R as an adjustable parameter. Also, in Ref. 3, the relaxation rate of propagation modes above the reservoir threshold was treated the same as the rate for propagation modes below this threshold. This is in error because longitudinal and fast transverse propagating modes that overlap the reservoir region will have shorter relaxation times owing to anharmonic processes which terminate in dispersive, or near-equilibrium, modes below them.

It was also assumed in Ref. 3 that N processes entirely within group 1 (the "NN processes") do not contribute to entropy production. The variational principle was invoked after making this hypothesis, and the conclusion reached that thermal resistance was independent of NN processes. In fact, this use of the variational principle is tautological. The entropy production rate summed over group-1 modes can be expressed as an integral over a non-negative integrand (Ref. 8, Ch. VII, Secs. 7 and 8). Thus, a complete cancellation of entropy production is possible only for a special set of distribution functions (quasiequilibrium or shifted distribution), and this is also the condition that $\partial N_q / \partial t \,|_{NN}$ vanishes (N_q is the occupation number of the mode with wave vector $\mathbf{q}$). All other distribution functions lead to entropy production. Therefore, the theory of Ref. 3 has merit where the dominant entropy production of N processes occurs in NR scattering, and NN scattering produces a relatively small effect.

The entropy production due to NN scattering in the Callaway approximation is calculated in the Appendix. It is shown there to be proportional to the difference between a direct and an inverse mean of the resistive relaxation time. This difference is greater, the greater the frequency dependence of the relaxation time. This brings out the need to include the effect of NN processes at low temperature when point-defect scattering is important. The discussion in the Appendix also confirms some earlier comments of Klemens[9] on circumstances under which N processes are important.

III. GENERALIZED TWO-FLUID MODEL

A. General scheme

The Boltzmann-Peierls equation for phonons can be written in the following approximate form:

$$-\frac{N_q - N(\beta)}{\tau_{NN}} - \frac{N_q - N_0}{\tau_R} = \mathbf{c}_q \cdot \nabla T \frac{dN_q}{dT} , \qquad (6)$$

where N_0 is the equilibrium occupation number, N_q the actual occupation number, $1/\tau_N$ is the single-mode relaxation rate obtained from Eq. (3), while $1/\tau_R$ denotes the relaxation rate due to all resistive processes. The term $N(\beta)$ in the first relaxation rate term is inserted to account for the return scattering terms $\Phi(\mathbf{q}'') - \Phi(\mathbf{q}')$ in Eq. (3). It has the form [see Eqs. (1) and (2)]

$$N(\beta) - N_0 = -(\mathbf{c}_q \cdot \nabla T)(\hbar\omega / T)(dN_0 / d[\hbar\omega])\beta , \qquad (7)$$

and in principle β is a function of ω. Since the operator (3) is an integral operator, Eq. (6) is an integral equation the solution of which is equivalent to finding the magnitude and frequency dependence of $\beta(\omega)$.

The Callaway approximation divides anharmonic processes into U and N processes, ascribes the effect of U processes to $1/\tau_R$, and chooses β, assumed independent of ω, so that N processes conserve momentum in the aggregate. In the previous two-fluid model,[3] the modes were divided into two groups: the propagating (nondispersive) modes for $\omega < \omega_P$ and the reservoir (dispersive) modes $\omega > \omega_R$, where generally $\omega_P > \omega_R$ and the region between ω_R and ω_P contains modes of both groups. For the propagating modes, it was assumed that $N(\beta) = N_q$ for N processes whose resultant (final) phonon has frequency less than ω_R. Those processes linking the propagating modes to the reservoir modes (resultant phonon with frequency greater than ω_R) called NR processes were counted towards $1/\tau_R$; viz., $N(\beta)$ was taken as N_0 for these processes. U processes were not explicitly considered. They were lumped in with the NR processes which have the same combination threshold requirement, and the sum of the two was represented by a modified Landau-Rumer[10] transition rate.

In that model, all modes were treated as having the same polarization and the same anharmonic relaxation rate, which is inconsistent in the frequency region $\omega_R \le \omega \le \omega_P$.

We now adopt a more realistic model in which there is a spectral range where longitudinal modes are propagating but transverse modes are dispersive. There are thus three spectral regimes as shown in Fig. 1: region 1, $\omega < \omega_R$, where all modes are propagating; region 1A, $\omega_R \le \omega \le \omega_P$, where longitudinal modes are propagating and transverse modes dispersive; and region 2, $\omega > \omega_P$ where all modes

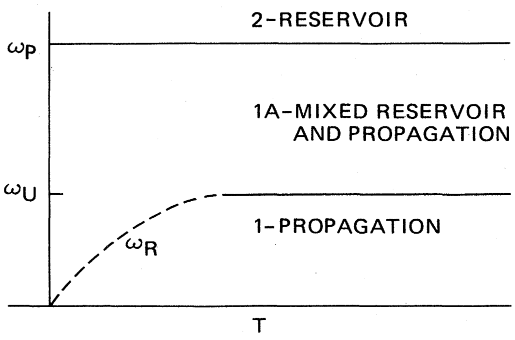

FIG. 1. Illustration of phonon propagation and reservoir spectral regions as a function of temperature.

are dispersive reservoir modes. Here ω_P is the highest frequency for which longitudinal modes have significant group velocity. Crystal isotropy is assumed throughout.

Furthermore, we combine the Callaway method and the two-fluid model as follows. We adopt Eq. (6) but assume that β is not constant but has constant values in three regimes as follows:

$$\begin{aligned}&\beta(\omega)=\beta \text{ for } \omega<\omega_R \text{ (region 1)},\\&\beta(\omega)=\beta' \text{ for } \omega_R\le\omega\le\omega_P \text{ (region 1A)},\\&\beta(\omega)=0 \text{ for } \omega>\omega_P \text{ (region 2)}.\end{aligned} \tag{8}$$

The theory thus contains three parameters β, β', and ω_R which must be determined, while ω_P is indicated by the form of the dispersion curves. Before discussing the method of determining β, β', and ω_R, one must determine how the various relaxation rates entering Eq. (6) are estimated.

B. *NR* process transition rate

We expect *NR* transitions, i.e., transitions transferring momentum from propagating to reservoir modes, to be dominated by processes in which a low-frequency mode ω combines with one of much higher frequency ω'. Since this is also the assumption of the Landau-Rumer[10] transition rate calculation, except that $\omega+\omega'$ must now exceed ω_R, we can modify that relaxation rate to

$$\tau_{NR}^{-1}=\frac{\gamma^2T\omega\pi}{4\rho v^2}\Delta C(\omega_R,\omega_C)\,, \tag{9}$$

where γ, the Gruneisen constant, is a measure of anharmonicity, ρ is the mass density, and v is the Debye average of the phonon velocity. The specific heat per unit volume C is broken up into spectral components, and $\Delta C(\omega_R,\omega_C)$ denotes the contribution to C from all the reservoir modes, i.e., modes for which $\omega_R\le\omega\le\omega_C$. Methods of calculating ΔC over various frequency domains and the temperature dependence of τ_{NR}^{-1} are discussed in Ref. 3.

Although Landau and Rumer considered only N processes explicitly, Eq. (9) also accounts for U processes if the locus of $\mathbf{q}'$ is defined in an extended zone scheme. The approximation made in (9) is that the locus of $\mathbf{q}'$, a cone in the nondispersive regime, maintains that shape to the highest spectral frequency ω_C, where the locus abruptly terminates. In reality, the locus is such that the half-angle of the cone gradually decreases, and vanishes when the group velocity of $\mathbf{q}'$ becomes small enough; the locus is thus a closed curve. Nevertheless, Eq. (9) is a reasonable approximation over a wide range of frequencies and temperatures; in particular, it leads to the correct high-temperature limit.

C. *NN* process transition rate

The *NN* processes are normal processes amongst the propagating modes. They contain processes such that all three modes are of comparable frequency (class 1c in the notation of Klemens[2]) as well as processes such that $\omega\ll\omega'\approx\omega''$ (class 1b in Klemens's notation) but $\omega'\approx\omega''<\omega_R$. Unless $\omega\ll\omega_R$, the only processes are of type 1c and of these the most important are those for which mode $\mathbf{q}$ splits into two modes $\mathbf{q}'$ and $\mathbf{q}''$ so that $\omega=\omega'+\omega''$. Following Klemens,[11] the transition rate for longitudinal phonons at low temperatures is

$$\tau_L^{-1}=\frac{3\pi}{4\sqrt{2}}(v_L/v_T)\frac{\gamma_1^2R(\hbar/k_B)\omega^5}{wv^2\omega_D^3}\times\left[1+\frac{2}{\exp[\hbar\omega/(2k_BT)]-1}+F(T)\right]. \tag{10}$$

Th first two terms in the large parentheses correspond to the N-process splitting rate where it is assumed that the phonon ω splits into two phonons of equal frequencies $\omega'=\omega''=\omega/2$. The Debye frequency is designated ω_D, v_L and v_T are the longitudinal and transverse sound speeds, respectively, w is the molecular weight, R is the gas constant, and γ_1 is a Gruneisen constant. The function $F(T)$ brings in the contribution of combination transitions, which was estimated by Klemens to be the same as for transverse phonons when $x=\hbar\omega/k_BT>1$. Thus, he used $F(T)=x^{-4}$ for $x>1$. For $x<1$, he used the Pomeranchuk formula for the longitudinal rate which is equivalent to $F(T)=40/x$.

For present purposes, we now estimate a mean rate for the transitions included in Eq. (10), in order to maintain the same level of polarization approximation as employed in Ref. 3. To do this, we take $\frac{1}{3}$ of the phonon splitting contribution to Eq. (10) since transverse phonons do not split, and use $F(T)=x^{-4}$ when $x>1$ now for both longitudinal and transverse combination processes. For $x<1$, we depart from the Pomeranchuk result used by Klemens, since we now want to include a transverse phonon contribution. Instead, we take, for $x<1$,

$$\tau^{-1}=(\pi\gamma^2T\omega/4\rho v^2)\Delta C(0,\omega_P) \tag{11}$$

as the *NN* contribution of phonon combination processes. This form of the Landau-Rumer result is an average over longitudinal and transverse contributions corrected for thermal phonon interactions.[12,13] The portion of τ^{-1} due to final-state modes between 0 and ω_R, which would be represented in the formula by the specific-heat factor $\Delta C(0,\omega_R)$, is the complement of the *NR* transition rate, Eq. (9). The portion between ω_R and ω_P has been added as an arbitrary correction for Klemens's class 1c transitions which are otherwise not included in the Landau-Rumer (1b) expression, as discussed above. The final formula for τ_{NN}^{-1}, therefore, becomes

$$\tau_{NN}^{-1}=\frac{\pi}{4\sqrt{2}}(v_L/v_T)\frac{\gamma_1^2R(\hbar/k_B)\omega^5}{wv^2\omega_D^3}\times\left[1+\frac{2}{\exp[\hbar\omega/(2k_BT)]-1}+G(T)\right]. \tag{12}$$

In this expression

$$G(T)=3/x^4,\quad x>1 \tag{13}$$

$$G(T)=\frac{\sqrt{2}\gamma^2 w(T_D/T)^3(v_T/v_L)\Delta C(0,\omega_P)}{\gamma_1^2 R\rho x^4}\,,\quad x<1 \tag{14}$$

so that this contribution to τ_{NN}^{-1} agrees with Eq. (11) when $x<1$, and with Klemens's $F(T)$ in Eq. (10) when $x>1$ (to within the polarization weighting factor).

D. Modified Callaway method

One now uses Eq. (6), but divides the frequency spectrum into three regions (with ω_R still to be specified). The following relaxation rates are used. In regions 1 and 1A, τ_N is given by Eq. (12), while τ_R is given by

$$\tau_R^{-1}=\tau_{NR}^{-1}+\tau_B^{-1}+\tau_I^{-1}\ . \tag{15}$$

Here τ_B^{-1} and τ_I^{-1} denote the rates for boundary and imperfection scattering, respectively, while τ_{NR}^{-1} is given by (9). Since it is assumed that all modes are in thermal equilibrium in region (2), Eq. (15) does not apply and the relaxation rates are not considered explicitly.

Equation (6) is now solved as in the Callaway method. The effective relaxation time $\alpha(\omega)$, defined by Eq. (2), is given by

$$\alpha=\tau_R+(\beta-\tau_R)\tau_c\tau_{NN}^{-1}\ . \tag{16}$$

This is simply a rearrangement of Callaway's result except that β has two different constant values in regions 1 and 1A. The combined transition rate τ_c^{-1} is defined as

$$\tau_c^{-1}=\tau_{NN}^{-1}+\tau_R^{-1}\ . \tag{17}$$

Callaway's results can be carried over, *mutatis mutandis,* to the present case to yield, for the conservation of quasimomentum in N processes that

$$\beta\int_0^{\omega_R}\tau_c\tau_{NN}^{-1}\tau_R^{-1}G_\omega d\omega+\beta'\int_{\omega_R}^{\omega_P}\tau_c\tau_{NN}^{-1}\tau_R^{-1}G_\omega d\omega =\int_0^{\omega_P}\tau_c\tau_{NN}^{-1}G_\omega d\omega\ . \tag{18}$$

The abbreviation

$$G_\omega\equiv\hbar\omega\frac{c^2(\nabla T/T)^2}{3}\frac{dN_q}{dT}D(\omega)\eta \tag{19}$$

has been introduced for compactness. The quantity $\eta D(\omega)$ is the density of nondispersive modes; η is the number of cells per unit volume and $\eta D(\omega)=\omega^2/2\pi^2c^3$.

E. Specification of β, β', and ω_R at low temperatures

At low temperatures, ω_R depends on T and must be determined consistently with Eq. (18), the momentum-conservation condition. However, this equation also contains β and β' so that additional conditions are needed. At high temperatures ω_R is determined simply by the dispersion of the transverse waves.

Since β and β' in Eq. (18) are averages of the effective relaxation times, we choose them to be proportional to average values of $\Phi(\mathbf{q}')+\Phi(\mathbf{q}'')$ in processes $\omega=\omega'+\omega''$ (splitting processes), and $\Phi(\mathbf{q}')-\Phi(\mathbf{q}'')$ in processes $\omega+\omega'=\omega''$ (combination processes). Since we are dealing with NN processes, and the most important cases are those for which ω is large, but still below ω_R, we focus on splitting processes. Now

$$\Phi(\mathbf{q}')+\Phi(\mathbf{q}'')=\hbar\mathbf{c}_q\cdot\nabla T[\omega'\alpha(\omega')+\omega''\alpha(\omega'')]/T\ . \tag{20}$$

We expect the phonon splitting rate to be strongest for processes centered about the symmetric case $\omega\rightarrow\omega/2+\omega/2$, in which case

$$\Phi(\mathbf{q}')+\Phi(\mathbf{q}'')=\hbar\mathbf{c}_q\cdot\nabla T\omega\beta/T\ . \tag{21}$$

We thus take β to be given by (21) at $\omega_R/2$, and β' by (21) at $\omega_P/2$. However, this procedure neglects the combination processes, which shift the average value of ω to somewhat higher frequencies. We therefore take

$$\beta=\alpha(\omega_R/\zeta)\ , \tag{22a}$$

$$\beta'=\alpha(\omega_P/\zeta)\ , \tag{22b}$$

where ζ is expected to be somewhat less than 2. Substituting this into Eq. (16) for the case when $\omega=\omega_R/\zeta$ and again when $\omega=\omega_P/\zeta$ one sees, after some cancellation, that

$$\beta=\tau_R(\omega_R/\zeta)\ , \tag{23a}$$

$$\beta'=\tau_R(\omega_P/\zeta)\ . \tag{23b}$$

Equations (23) can now be substituted into the momentum-conservation condition (18) to yield

$$\tau_R(\omega_R/\zeta)\int_0^{\omega_R}\tau_c\tau_{NN}^{-1}\tau_R^{-1}G_\omega d\omega +\tau_R(\omega_P/\zeta)\int_{\omega_R}^{\omega_P}\tau_c\tau_{NN}^{-1}\tau_R^{-1}G_\omega d\omega=\int_0^{\omega_P}\tau_c\tau_{NN}^{-1}G_\omega d\omega\ . \tag{24}$$

If ζ is chosen, this condition determines ω_R as a function of temperature. However, it is also necessary to choose a value of the parameter ζ. This parameter will be chosen empirically, independent of T and of defect concentration to give an optimum overall fit.

As the temperature is increased, ω_R reaches ω_U, which is governed by the dispersion of the transverse waves. Above this temperature, Eqs. (23) can no longer be used. Instead, we set $\omega_R=\omega_U$, then assume that $\beta=\alpha(\omega_U/\zeta)$ and use (18) to obtain β'.

IV. APPLICATION TO LiF

A. Computational procedures

Equations (8) and (A8) of the Appendix provide the formula for the thermal conductivity κ:

$$\kappa=\frac{k_B(k_BT/\hbar)^3}{8\pi^2 v}\left[\int_0^{x_P}\frac{\tau_R t^4dt}{\sinh^2(t/2)}+\int_0^{x_R}\frac{(\beta-\tau_R)\tau_c t^4dt}{\sinh^2(t/2)\tau_{NN}}+\int_{x_R}^{x_P}\frac{(\beta'-\tau_R)\tau_c t^4dt}{\sinh^2(t/2)\tau_{NN}}\right]. \tag{25}$$

The transition rates τ_R^{-1}, τ_c^{-1}, and τ_{NN}^{-1} are defined by Eqs. (9), (12), (15), and (17), with $\tau_I^{-1}=AT^4x^4$, where A is the Rayleigh scattering strength for isotope plus impurity scattering. A dislocation scattering term was included in τ_R^{-1} and its effect tested in the course of the computations. No improvement ensued in the fits obtained, so it was not used in the final calculations. This finding undoubtedly reflects the success of Thacher's program[14] to reduce dislocation densities in his specimens.

Equation (25) was reduced to the form of Eq. (45) of Ref. 3 for computational purposes and integrated by the same 48-order Gaussian quadrature scheme used in the previous work. The calculations, programmed in FORTRAN, were carried out interactively as in Ref. 3.

The iteration to determine x_R was carried out as follows. For temperature close to or below a point where x_R may equal x_U, an iteration was performed with the starting value $x_R=x_U$. The various transition rates were computed for this starting value along with β' according to Eq. (23b). A value of β was then computed from Eq. (18). From this β, a corrected $x_R=x_R(\text{new})$ was computed from Eq. (23a) and compared to the starting value. If the new value differed from the starting value by more than $\Delta x=1.0\times10^{-3}$, another calculation was performed beginning with $x_R(\text{start})=\frac{1}{2}[x_R(\text{new})+x_R(\text{old})]$. This procedure converged for all the LiF cases. The final value of x_R obtained was then compared to x_U to determine whether or not this frequency lay in the low- or high-temperature reservoir region. If x_R so obtained was greater than x_U, it was reset to x_U, and the computation of the transition rates and betas repeated, followed by the computation of κ.

B. Comparison with experiment

Computations were carried out for four of Thacher's[14] LiF specimens of varying isotopic purity which had been annealed to reduce the dislocation concentration. The specimens are those whose thermal conductivities are denoted (A), (B), (C), and (D) in Fig. 4 of Ref. 14. Table I lists the lattice characteristics of LiF used in the calculation. The Debye temperature $T_D=700$ K was selected as a compromise between low- and high-temperature values. The computation was not very sensitive to its value except, of course, for adjustment of the boundary length $\Lambda_B=v\tau_B$. The value of the frequency $\nu_c=\omega_c/(2\pi)$ was selected from spectral data,[15] and the sound speed ratio v_L/v_T was taken from Anderson.[16] The remaining parameters were inferred from the fitting process. We note that ν_U, ν_P, and γ, which appear in the theory of Ref. 3 are hardly changed from the values 5.46, 10.9, and 1.45, respectively, inferred there. This is reassuring, since that theory should still be a good first approximation. The value of $\zeta=1.725$ is reasonably close to 2, the value it would have if all phonons split equally in the absence of combination transitions.

The value inferred for γ from the NR transitions is slightly lower at 1.36 than the value 1.45 inferred in Ref. 3. This is substantially lower than the experimental value[17] which ranges from 1.6 at room temperature down to 1.7 at 0 K. This result suggests that the NR rate overestimates the true resistive transition rate; viz., some of the momentum supplied by the NR processes is not completely balanced by resistive processes, but is conserved and passed on to other modes. Such an effect is reasonable in view of our crude approximations to the return flow back to a given state, and would improve in an iterative computation of $\Phi(\mathbf{q})$ to replace the constant β and β' values used in the present calculation. The value 1.758 inferred for γ_1, in contrast, falls close to the low-temperature end of the experimental range.

Table II lists the extrinsic parameters used in the computation. For case (A), the Rayleigh strength A was inferred from the fit to the data since the isotope scattering as given by Thacher is below the impurity scattering level. For the remaining cases, Thacher's theoretical values were used. The Casimir boundary lengths $\bar{\Lambda}_B$ inferred from the fit primarily reflect the choice of T_D and are, therefore, different from Thacher's. They may also be influenced by near-surface dislocations (as discussed by Thacher).

Figure 2 shows the results of the computations. For curve A, the agreement between the theoretical curve and the data is considerably better than that obtained in Ref. 3, especially in the vicinity of 20—30 K (the steepness of the curve in the region along with the inaccuracies of curve drawing make the comparisons of Fig. 4 of Ref. 3 appear somewhat better than they actually are). Typical differences are about 2% with a maximum error of 6%. This level of agreement suggests that most of the possible sources of discrepancy cited in Ref. 3, such as temperature variations of T_D and γ, are less important than the error caused by the previous neglect of NN processes. The overall fits for specimens (B), (C), and (D) are superior to that obtained in Ref. 3 for the comparable Berman-Brock data analyzed there, with the fit for curve (D) being

TABLE I. Lattice characteristics of LiF used in the calculation. T_D is the Debye temperature in K, ν_U is the high-temperature (U-process) reservoir threshold frequency, ν_P is the propagation mode upper limit, and ν_C is the crystal phonon spectrum upper frequency limit, all in THz. The Grüneisen constants γ and γ_1 are used in the anharmonic transition rates for combination transitions and phonon splittings, respectively. The parameter ζ is used to relax the assumption that all phonons split into two phonons of equal frequency. The longitudinal and transverse sound speeds are denoted v_L and v_T, respectively. The sound speed ratio along with ν_C was obtained from experimental data, while the remaining parameters were inferred from the fits to the Thacher thermal-conductivity data.

T_D (K)	ν_U	ν_P	ν_C	γ	γ_1	ζ	v_L/v_T
700	5.40	10.5	20.0	1.36	1.758	1.725	1.62

TABLE II. Specimen characteristics of the LiF samples (A), (B), (C), and (D), of Fig. 4 of Ref. 14 used in the present analysis. $\overline{\Lambda}_B$ is the Casimir boundary length in mm and A is the Rayleigh scattering strength in $\sec^{-1}\,K^{-4}$. The value of A listed in parentheses was inferred from the fit. The others are theoretical values given by Thacher.

	(A)	(B)	(C)	(D)
$\overline{\Lambda}_B$	8.8	6.8	6.2	6.0
A	(0.0189)	0.126	0.318	1.2

the poorest. Curves (B), (C), and (D) show distinct cusps at two temperature points; these are artifacts of the approximations employed. The higher-temperature cusps are due to the discontinuous onset of the low-temperature reservoir conditions (or, equivalently, the discontinuity in beta). The cusps appearing near 15 K were determined by numerical experimentation to arise from the discontinuity at $x=1$ in the function $G(T)$ used to estimate τ_{NN}^{-1} in Eq. (12). Curve (D), e.g., was quite sensitive to the position of this discontinuity and the magnitude of $G(T)$ on either side of it. This behavior suggests that the error in $G(T)$, viz., the phonon combination contribution to τ_{NN}^{-1} is the dominant error in the present formulation.

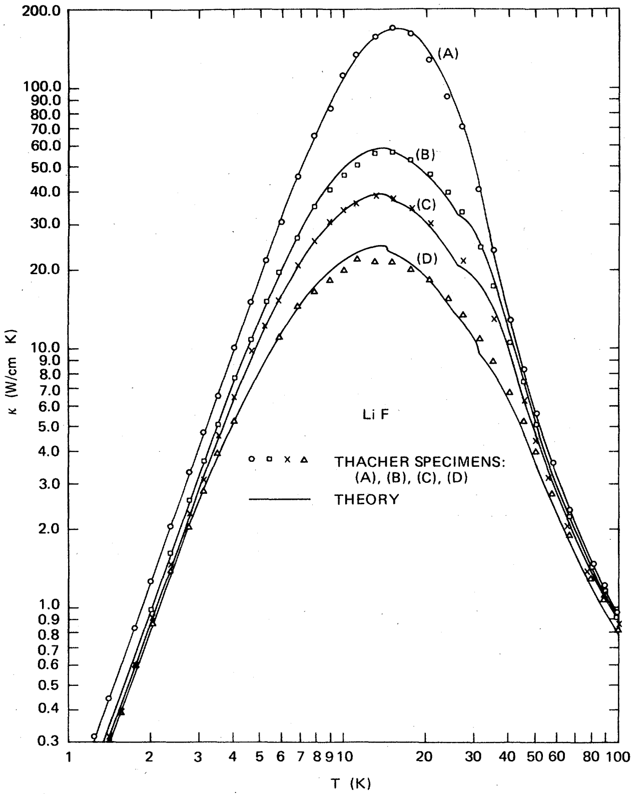

FIG. 2. Comparison of theory and experiment for four of Thacher's LiF specimens with different isotopic concentrations. Only the Rayleigh scattering strength is adjusted among the four theoretical curves. Cusps are artifacts of the approximations employed.

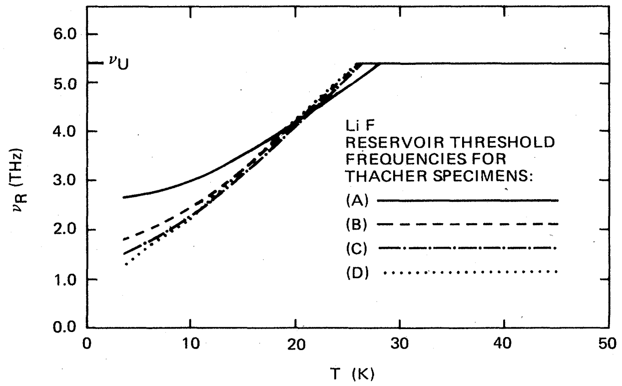

FIG. 3. Reservoir threshold frequency ν_R as a function of temperature for the four Thacher LiF specimens whose thermal conductivity is shown in Fig. 2.

Figure 3 shows the reservoir threshold frequency $\omega_R/(2\pi)$ as a function of temperature for the four cases. The intersection of the low- and high-temperature reservoirs occur at 28.2, 26.1, 25.9, and 25.7 K, respectively, for cases (A), (B), (C), and (D). The fact that the purest case has the highest intersection temperature with the extrinsic reservoir seems surprising, but it is difficult to draw conclusions on this feature in view of the small magnitude of the effect and the error in our approximations for β, β', and τ_{NN}^{-1}, as mentioned above. Below about 15 K, the four reservoir boundaries behave qualitatively as expected from the interpretation of the extrinsic reservoir advanced in Ref. 3.

The Callaway β correction to the purely resistive thermal conductivity, viz., the second term of Eq. (25), is commensurate with the resistive contribution κ_R (the first term) at the peak of κ, and drops rapidly in both directions away from the peak. The peak points of the Thacher data set at 15, 15, 13, and 11.2 K, respectively, for curves (A), (B), (C), and (D), have κ/κ_R equal to 0.64, 0.46, 0.55, and 0.67. This difference between κ and κ_R drops to less than 10% at 50 K in all four cases.

The contribution of the β' correction to κ [the third term of Eq. (26)] is relatively small. From the point of onset of the low-temperature reservoir conditions ($\sim$26 K) downward in T, the ratio of this correction to the total κ is generally 10^{-1} or less. From this point upward in T it stays relatively constant with gradual decrease after 300 K. The β' correction to κ is negative in all cases computed, in contrast to the β correction [the second term of Eq. (25)]. The latter correction is positive above about 45 K and negative below for all cases.

The behavior of β' relative to β is interesting. Toward low T, of course, $\beta\rightarrow\tau_B$. Similarly, β' has a low-T limit by virtue of Eq. (23b), viz., $\beta'\rightarrow\tau_I(\omega_P/\zeta)$ because the contribution of τ_{NR} to τ_R dies out. This limit is reached in all four cases just on the high-temperature side of the peak of κ. Starting from this low-temperature asymptote, β/β' increases with T toward a high-temperature asymptote which can be obtained from Eqs. (18) and (23a). If we set $\tau_c\simeq\tau_{NN}$ and make use of the simple limiting forms of the Debye integrals for $x \ll 1$, the result obtained for this asymptote is

$$\beta'/\beta \rightarrow \frac{4\omega_P^3\omega_R/(3\zeta)-\omega_R^4}{(\omega_P^4-\omega_R^4)} . \qquad (26)$$

This ratio has the value 0.357 with ω_P, ω_R, and ζ as inferred herein. This high-T asymptote was reached at ~ 100 K for cases (B), (C), and (D).

In the purest case β' is always positive, whereas in the other three cases it goes negative just above the low-temperature reservoir region over the brief span of temperature from about 25—30 K. It then recovers to a positive value over the range 35—45 K, and toward higher temperature, increases toward equality with the pure case. Such negative values of β' are physically unrealistic since they correspond to phonon drift from low to high temperature. They indicate that $\tau_R(\omega_R/\zeta)$ which has been used to estimate β in Eq. (18) is too large for momentum conservation to be achieved. But, the effect is sufficiently small that we neglect it in order to avoid further adjustable parameters or *ad hoc* assumptions.

Of all the cases treated in Ref. 3, the new theory has been applied only to LiF because this is the crystal where not only is point scattering strong, but where it has been varied in a controlled manner. These LiF measurements present, therefore, the most stringent test of the theory. With the new criterion for choosing ω_R and the use of two values of β, the overall fit is improved while, at the same time, the physics of the problem is clarified.

When more accurate transition rates for phonon decay and type-1c combination processes become available, the parameter ζ and the arbitrary treatment of combination processes in τ_{NN}^{-1} can be dispensed with. More complete spectral data should also permit ω_U and ω_P to be stipulated from the data rather than treated as adjustable.

VI. CONCLUSION

The two-fluid phonon theory of Ref. 3 has been extended to account for the effects of NN transitions ignored in that approach. The corrected theory (basically now a "three-fluid" theory) is capable of explaining thermal-conductivity behavior through the region of peak value with considerable accuracy in the purest cases. The analysis also succeeds in identifying dominant phonon transitions and their roles in determining thermal resistivity. Phonon transition-rate formulas of acoustic attenuation theory are seen to be valid for thermal conductivity as well, when account is made for the dispersive structure of high-frequency spectral branches, although a more accurate N-process transition rate is still needed for combination processes involving only phonons in the propagation region and for phonon decays. Once phonon modes are separated according to dispersiveness and departure from thermal equilibrium, and accurate forms of the dominant transition rates obtained, it should be possible to solve the Peierls-Boltzmann integral equation[1] in a straightforward numerical manner. That is to say, the new approach appears to offer the necessary framework for a fundamental systematic approximation to this integral equation such as, e.g., an iterative method of the type employed in photon transport theory.[7]

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APPENDIX A: N-PROCESS AND ENTROPY PRODUCTION RATES IN THE TWO-FLUID MODEL

We consider a simplified crystal with a single acoustic branch with constant velocity for wave numbers $0<q<q_P$ and a maximum frequency ω_P. For wave numbers $q>q_P$, there are some modes of zero group velocity and frequency ω_P. In addition, there may be optic modes of zero group velocity above ω_P. This special model permits some general arguments without the complications of the overlap region between the lowest transverse acoustic and the highest longitudinal acoustic Brillouin zone boundary modes.

The zero-group-velocity acoustic and optic modes are assumed to be in thermal equilibrium; their small deviation functions $\Phi(\mathbf{q})$ vanish. Therefore, these modes constitute high-temperature reservoir modes in the sense of Ref. 3. All modes below ω_P (region 1) will contribute to propagation of heat, and since reservoir modes (region 2) have frequency $\omega \geq \omega_P$, the high-temperature reservoir boundary frequency ω_R for this model coincides with ω_P. The total three-phonon anharmonic scattering rate becomes

$$-\left.\frac{\partial N_q}{\partial t}\right|_{AN} = \int_{\mathbf{q}'(1)}[\Phi(\mathbf{q})+\Phi(\mathbf{q}')-\Phi(\mathbf{q}'')]P(\mathbf{q},\mathbf{q}';\mathbf{q}'')d^3q' + \int_{\mathbf{q}'(2)}[\Phi(\mathbf{q})+\Phi(\mathbf{q}')-\Phi(\mathbf{q}'')]P(\mathbf{q},\mathbf{q}';\mathbf{q}'')d^3q'$$
$$+\tfrac{1}{2}\int_{\mathbf{q}'(1)}[\Phi(\mathbf{q})-\Phi(\mathbf{q}')-\Phi(\mathbf{q}'')]P(\mathbf{q}',\mathbf{q}'';\mathbf{q})d^3q' , \qquad (A1)$$

where P, defined in Ref. 8, is a transition rate which includes a resonance factor restricting transitions as described after Eq. (3) of the text. The first two terms of Eq. (A1) correspond to combination transitions while the third term is due to phonon splitting transitions.

The notation $\mathbf{q}'(1)$ under the integral signs indicates the collection of all modes below ω_P (wherein all propagation of heat takes place). Modes $\mathbf{q}'$ and $\mathbf{q}''$ in the first integral of Eq. (A1), viz., those modes with which $\mathbf{q}$ interacts in combination processes, are restricted to this lower region.

The group of modes designated $\mathbf{q}'(2)$ under the second integral constitute those modes with wave number greater than q_P or optic modes; $\mathbf{q}'$ and $\mathbf{q}''$ here are restricted to this reservoir group. Because of the assumption of thermal equilibrium beyond $\mathbf{q}_P$, $\Phi(\mathbf{q}')$ and $\Phi(\mathbf{q}'')$ will vanish over modes $\mathbf{q}'(2)$, and the second integral of Eq. (A1) becomes a single-mode relaxation rate expression. Those transitions for which $q' < q_P$ and $q'' > q_P$ will be lumped with those for which q'' lies below q_P. Since these transitions will primarily belong to Klemen's class 1c,[2] this approximation should not introduce much error.

For this primitive "two-fluid" model, the first and third integrals of Eq. (A1) constitute the scattering rate designated $(\partial N_q/\partial t)_{ANN}$ in Ref. 3 and herein shortened to $(\partial N/\partial t)_{NN}$. These terms are due to N processes only. The second integral of Eq. (A1), designated $(\partial N/\partial t)_{NR}$, includes in principle both N and U processes, but because of the validity of the single-mode expression, all transitions contributing to this rate behave as purely resistive processes so that there is no need to distinguish between them.

In the Callaway[4] approach one writes

$$\Phi(\mathbf{q}') = -\hbar\omega'\beta\mathbf{c}_q \cdot \nabla T/T \tag{A2}$$

and similarly for $\Phi(\mathbf{q}'')$, and it is assumed that β is common to both expressions. This replacement is made for modes $\mathbf{q}'$ and $\mathbf{q}''$, but not for mode $\mathbf{q}$ in the first and third integrals of Eq. (A1). One then treats β as a frequency-independent parameter to be determined by the condition that the sum of all N processes conserves total phonon momentum. We now make the Callaway approximation only for the NN processes, treating NR processes (normal processes with $\mathbf{q}''$ in the reservoir modes) by means of the second integral in Eq. (A1), but taking $\Phi(\mathbf{q}') = \Phi(\mathbf{q}'') = 0$. That is to say, treating these NR processes in terms of a single-mode relaxation time. We thus have a Callaway-type linearized Boltzmann equation as given by Eq. (6) of the text with τ_N^{-1} taken as τ_{NN}^{-1}, and where τ_R^{-1}, the transition rate for modes in region 1 due to all processes other than NN processes, is given by Eq. (15) of the text.

The essence of the Callaway approximation is that β, a measure of the disequilibrium toward which N processes tend to drive modes of frequency ω, is assumed to be the same for modes of all ω, and the value of β is chosen so that the total momentum of the phonon gas is unchanged by the sum of all N processes. Callaway's results can be immediately translated to the present theory and a correction obtained for the NN processes. Using his notation, we have

$$N_q - N_0 \equiv -\alpha\mathbf{c}_q \cdot \nabla T \frac{dN_q}{dT} , \tag{A3}$$

$$N_q - N(\beta) \equiv -(\alpha - \beta)\mathbf{c}_q \cdot \nabla T \frac{dN_q}{dT} . \tag{A4}$$

The "effective relaxation time" $\alpha(q)$ obeys the relation

$$\alpha = \tau_c(1 + \beta/\tau_{NN}) , \tag{A5}$$

where $\tau_c^{-1} = \tau_{NN}^{-1} + \tau_R^{-1}$.

The condition of conservation of phonon momentum imposed on β determines it to be

$$\beta = \frac{\int_0^{\omega_P} \tau_c \tau_{NN}^{-1} G_\omega d\omega}{\int_0^{\omega_P} \tau_c \tau_{NN}^{-1} \tau_R^{-1} G_\omega d\omega} . \tag{A6}$$

The abbreviation G_ω is defined by Eq. (19) of the text.

The total entropy production rates can be shown to be[8]

$$\dot{S} = \int_0^{\omega_P} \alpha G_\omega d\omega , \tag{A7}$$

and this yields the thermal conductivity $\kappa = \dot{S}/(T/T)^2$. One readily sees that this is equivalent to the usual kinetic theory formulation of κ. Equation (A7) can now be rearranged into the form of Eq. (16) of the text in order to separate the purely resistive effects from the NN process effects. With this rearrangement, $\dot{S}$ becomes

$$\dot{S} = \int_0^{\omega_P} \tau_R G_\omega d\omega + \int_0^{\omega_P} (\beta - \tau_R) \tau_c \tau_{NN}^{-1} G_\omega d\omega , \tag{A8}$$

such that the first term is the result as obtained in Ref. 3, and the second term constitutes a correction for the NN scattering. Calling this correction term $\Delta\dot{S}$, Eqs. (A6) and (A8) lead to

$$\Delta\dot{S} = \frac{\left[\int \tau_c \tau_{NN}^{-1} G_\omega d\omega \right]^2 - \int \tau_R \tau_c \tau_{NN}^{-1} G_\omega d\omega \int \tau_R^{-1} \tau_c \tau_{NN}^{-1} G_\omega d\omega}{\int \tau_R^{-1} \tau_c \tau_N^{-1} G_\omega d\omega} . \tag{A9}$$

We now appeal to the Schwartz inequality to show that $\Delta\dot{S}$ is negative, as we expect it must be because it represents additional scattering beyond τ_R^{-1} and, hence, causes a reduction in the thermal conductivity.

For appropriately integrable functions $y(\omega)$ and $z(\omega)$ (which we assume the functions involved in the present analysis to be) the Schwartz inequality[18] states that

$$\int y^2 d\omega \int z^2 d\omega \geq \left[\int yz \, d\omega \right]^2 . \tag{A10}$$

The choice

$$y \equiv (\tau_R \tau_c \tau_{NN}^{-1} G_\omega)^{1/2}, \quad z \equiv (\tau_R^{-1} \tau_c \tau_{NN}^{-1} G_\omega)^{1/2} \tag{A11}$$

shows the numerator in Eq. (A9) to be negative. Since the denominator is positive, it follows that

$$\Delta\dot{S} \leq 0 . \tag{A12}$$

From Eq. (A9) we see that the correction term introduced by the NN processes depends upon the difference between a direct and an inverse mean of τ_R (where the inverse mean is always smaller). This difference will be greater, the stronger the ω dependence of τ_R. Conversely, $\Delta\dot{S}$ vanishes for an ω-independent τ_R as the Schwartz inequality passes over into an equality in this limit. Therefore, the nearer τ_R is to being independent of phonon frequency within group 1, the smaller will be the value of $\Delta\dot{S}$, viz., the less effective the *NN* processes become. This result provides an alternative basis for the statement made much earlier by Klemens[9] that *N* processes are most important in the presence of strongly-frequency-dependent resistive scattering. He has also pointed out that the difference between the direct and inverse means is small for a linearly-frequency-dependent transition rate. Thus, we expect $\Delta\dot{S}$ to be relatively small as long as the linear τ_{NR}^{-1} adopted in the text and in Ref. 3 is the dominant resistive rate.

We can also show that the Callaway approximation preserves the non-negative character of the *N*-process entropy production rate. For the subset of *NN* processes this rate is given by

$$\dot{S}_{NN} = T^{-1} \sum_{(1)} \Phi(q) \frac{N_q - N(\beta)}{\tau_{NN}} , \qquad \text{(A13)}$$

where the summation as indicated is taken over group-1 modes. Conversion to integral form and elimination of Φ in terms of α by means of Eq. (2) of the text yields

$$\dot{S}_{NN} = \int_{(1)} \frac{\alpha(\alpha-\beta)}{\tau_{NN}} G_\omega d\omega . \qquad \text{(A14)}$$

It is straightforward to show that the choice of $y \equiv (\tau_{NR}^{-1} G_\omega)^{1/2}$ and $z \equiv \alpha(\tau_{NN}^{-1} G_\omega)^{1/2}$ in the Schwartz inequality leads to $\Delta\dot{S}_{NN} \geq 0$, when β is expressed in the form

$$\beta = \int \alpha \tau_{NN}^{-1} G_\omega d\omega \left[\int \tau_{NN}^{-1} G_\omega d\omega \right]^{-1} . \qquad \text{(A15)}$$

The preceding arguments follow through for the original Callaway theory by replacing τ_{NR}^{-1} and τ_{NN}^{-1} by the *U*- and *N*-process transition rates, respectively.

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