

Thermal Conductivity of LiF and NaF and the Ziman Limit*

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A model calculation of lattice thermal conductivity is presented and applied to measurements on LiF and NaF crystals of high purity. The treatment is in the spirit of a Callaway analysis, but at a somewhat more fundamental level: The Ziman variational principle for thermal conductivity derived from the phonon Boltzmann equation is used, with the phonon distribution function approximated by a displaced Planck part plus another term reducing the deviation from equilibrium for high-frequency phonons. An isotropic Debye approximation for the phonon spectra of LiF and NaF gives a good fit to the conductivity data, with only two semi-adjustable parameters (Grüneisen constant and a zone-edge longitudinal phonon frequency) for the anharmonic contribution. The most important feature of the calculation is the failure of the thermal conductivity to approach the Ziman limit of resistanceless phonon-phonon N processes. This is due to the important role played by high-frequency phonons in thermal conduction. Even for an infinite perfect crystal at arbitrarily low temperatures, the Ziman limit underestimates the conductivity by at least 50%. If this prediction is correct, it is not a peculiarity of LiF and NaF alone, and should be of importance for the theory of second-sound propagation in insulators.

I. INTRODUCTION

In discussions of the lattice thermal conductivity of relatively pure insulators, the following assumption is usually made: As the temperature is lowered, phonon-phonon umklapp processes become increasingly frozen out in comparison with the much more rapid normal processes, so that eventually the normal processes alone must determine the way in which the energy transported through the lattice is distributed among the phonons. This is the Ziman limit.^{1,2} One finds that the thermal conductivity in this limit is independent of the (essentially infinitely rapid) normal-process collision rates. The Ziman limit is a theoretical limit; any experimental evidence that it is ever approached or achieved is always indirect. The theoretical evidence is meager. First-principles calculations of the thermal conductivity in the Ziman limit have been performed only for rare-gas crystals,³ and appear to come out low. Such appearances are however obscured by uncertainties in parameters of the interatomic potential.

In this work we present model calculations of lattice thermal conductivity, which when applied to high-purity LiF and NaF crystals give the same information as a Callaway analysis⁴ but with fewer, more interpretable adjustable parameters. The thermal conductivity of the model does *not* approach the Ziman limit, for reasons sketched in Sec. II. This is not an academic point; in both experiments to be examined, at temperatures as low as $T \approx \frac{1}{18} \Theta_D$, the thermal resistance due to defects and impurities is still demonstrably negligible, so if the Ziman limit is valid at all it should be achieved in these cases. The model calculation, however,

predicts a conductivity more than 50% higher than the Ziman limit at these temperatures.

More importantly, though, the validity of the Ziman limit is *assumed* in the hydrodynamic theory of second-sound propagation in insulators.^{2,5} It seems clear that the theory is really not critically dependent upon this assumption, but it will lead to quantitative inaccuracy: The second-sound damping rate due to thermal conduction is clearly affected, and so is that due to viscosity, which should have a non-negligible contribution from umklapp processes. This would of course lead to extra dispersion in the second-sound velocity when the damping due to either mechanism is large, but even in regions of small damping the propagation velocity will not be that of "drifting" second sound if the Ziman limit is never completely achieved.⁵ Second-sound propagation is not discussed in this work, but it is felt that the question of the validity of the Ziman limit is at least as relevant to the analysis of recent second-sound data^{6,7} in NaF as it is to the thermal conductivity.

II. MOTIVATION

In this work we emphasize the role of *high-energy* phonons in thermal conduction. The argument of the work is this: Consider phonons of energy $\hbar\omega \gg kT$ which belong to a high-frequency branch of the phonon spectrum. Then, (a) normal- and umklapp-process relaxation times τ^N and τ^U for these modes, in the single-mode relaxation time approximation,⁸ are independent of temperature. (b) Because of (a), such phonons can make the same size contribution to the thermal resistance as "thermal" phonons (those with $\hbar\omega \approx kT$), upon which previous treatments have concentrated. (c)

The contribution of high-energy phonons to the thermal resistance is not correctly given by the Ziman limit, because $\tau^N \approx \tau^U$ for these modes.

To motivate point (a), observe that if the phonon energy $\hbar\omega \gg kT$, the dominant attenuation mechanism for the phonon is the anharmonic decay into two other phonons of energy $\sim \frac{1}{2}\hbar\omega$. Whatever their relative sizes, both normal- and umklapp-process decay rates will be temperature independent, corresponding to spontaneous emission, but the emission process is only allowed if the original high-energy phonon belongs to a high-frequency branch of the phonon spectrum. For instance, high-energy longitudinal phonons will decay spontaneously via the processes $l-t+t$ and $l-l+t$. Orbach and Vredevoe⁹ have considered the *normal*-process contributions to these decays, but we shall argue that if the longitudinal phonon has a large enough wave vector the decay process can just as easily be umklapp as normal.

Point (b) amounts to asserting that the very small portion of the heat current carried by high-energy phonons is attenuated so rapidly that these modes develop much of the thermal resistance. Consider a typical thermal phonon, called 1; $\hbar\omega_1 \approx kT$. For low enough temperatures, phase-space considerations dictate that the dominant attenuation mechanism for this phonon is an absorption process, $1+2 \rightarrow 3$. Ziman points out¹ that only the *umklapp* absorption process is expected to contribute significantly to the thermal resistance, and the transition rate for that process is dominated by a factor $\exp(-\hbar\omega_2/kT) \approx \exp(-\hbar\omega_3^{\text{min}}/kT)$ owing to the exponentially small number of available 2 phonons of high enough energy to make the U process allowed, which requires that phonon 3 be on a high-frequency branch with $\hbar\omega_3 \geq \hbar\omega_3^{\text{min}} \gg kT$. The resulting contribution of thermal phonons to the thermal resistance is dominated by the familiar dependence $\exp(-\hbar\omega_3^{\text{min}}/kT)$.

Now turn things around and consider a high-energy phonon like 3 above. It attenuates via $3 \rightarrow 2+1$ (neither 1 nor 2 need be thermal phonons, though), and point (a) above applies. The temperature dependence of the contribution of such high-energy phonons to the resistance is thus determined not by the temperature dependence of the relaxation time, but of the heat capacity, which varies like $e^{-\hbar\omega_3/kT}$. Summing over high-energy phonons, one thus expects a resistance dominated by $\exp[-\hbar\omega_3^{\text{min}}/kT]$, i. e., the *same* temperature dependence as the contribution of thermal phonons. Are the *magnitudes* of the two contributions also similar? One must now delve into phase-space integrals; for the model of Sec. III they are.

To motivate point (c), we first remark that if it is indeed true that spontaneous-emission lifetimes satisfy $\tau^N \approx \tau^U$, then U processes *never* become

frozen out for high-energy modes, and will always compete with N processes in determining how the heat current is distributed over the phonons. Thus the argument for the Ziman limit given in the Introduction breaks down.

The point about lifetimes is simply that if phonon 1 has a large enough wave vector, then the decay process $1 \rightarrow 2+3$ can just as easily be umklapp as normal. In fact one quite generally expects the relation $\tau^N \ll \tau^U$, which the Ziman limit assumes is valid for all phonons, to be violated *near* the surface of the Brillouin zone, simply because one must have $\tau^N \geq \tau^U$ on a considerable portion of the zone surface. To prove this latter assertion, focus attention on a phonon with wave vector \vec{q}_1 on that face of the zone surface which bisects the reciprocal lattice vector \vec{G}_1 . We shall show that *if* the vector $\vec{q}_1 - \vec{G}_1$ is in the star of \vec{q}_1 , then to every allowed normal process, for which

$$\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0, \quad (1)$$

there corresponds an allowed umklapp process of form

$$\vec{q}_1 + \vec{q}'_2 + \vec{q}'_3 = \vec{G}_1, \quad (2)$$

which makes the same contribution to τ^U as (1) does to τ^N . Since (1) exhausts all N processes but (2) does not exhaust all U processes (other \vec{G}' 's than \vec{G}_1 are almost always allowed), we conclude $\tau^U_{\vec{q}_1 s_1} \leq \tau^N_{\vec{q}_1 s_1}$. Here s_1 denotes the polarization branch.

Operate on (1) with some operation R of the point group of the lattice:

$$R\vec{q}_1 + R\vec{q}_2 + R\vec{q}_3 = 0. \quad (3)$$

Choose R such that $R\vec{q}_1 = \vec{q}_1 - \vec{G}_1$. Then (3) can be written

$$\vec{q}_1 + R\vec{q}_2 + R\vec{q}_3 = \vec{G}_1, \quad (2')$$

which is Eq. (2). The contribution of (2') to the single-mode⁸ relaxation time $\tau^U_{\vec{q}_1 s_1}$ depends on the \vec{q}' 's and polarizations only through the polarization vector $\vec{e}_{\vec{q}_1 s_1}$, frequency $\omega_{\vec{q}_1 s_1}$, the factors $e^{i\vec{q}_1 \cdot \vec{l}}$, where \vec{l} is a direct lattice vector, and similar quantities for $(R\vec{q}_2, s_2)$ and $(R\vec{q}_3, s_3)$. None of these quantities are changed by replacing \vec{q}_1 by $\vec{q}_1 - \vec{G}_1$ (the polarization vector may at most change sign, which does not affect the final result). Further, we can replace $\vec{q}_1 - \vec{G}_1$ by $R\vec{q}_1$ and then $R\vec{q}_1, R\vec{q}_2, R\vec{q}_3$ by $\vec{q}_1, \vec{q}_2, \vec{q}_3$ without changing the contribution; the last replacement merely corresponds to evaluating a coupling constant in a rotated direct lattice. But now one is evaluating the contribution of process (1) to $\tau^N_{\vec{q}_1 s_1}$. Thus we have the desired result.

For the fcc direct lattice, the portion of the Brillouin-zone surface on which $\vec{q}_1 - \vec{G}_1$ is in the star of \vec{q}_1 consists of the entire surface of the square faces and the points at the centers of the hexagonal faces.

For the bcc and simple cubic lattices, it consists of the entire zone surface.

The considerations of this section are certainly not definitive, but our object is merely to provide a reasonable motivation for the variational ansatz (18) of Sec. III.

III. VARIATIONAL PRINCIPLE; TRIAL FUNCTIONS

The quantum state of an insulating crystal is specified by the number of phonons N_1 in each mode $\vec{q}_1 s_1$, which we write as a part corresponding to thermal equilibrium plus a deviation n_1 from equilibrium, imagined small:

$$N_1 = (e^{\beta \hbar \omega_1} - 1)^{-1} + n_1, \quad (4)$$

where $\beta = 1/kT$.

In a wave-packet description, the space and time dependence of N_1 is governed by the linearized phonon Peierls-Boltzmann equation. To discuss the steady-state deviation from equilibrium caused by a uniform temperature gradient $\vec{\nabla}T$, one can put the equation in the form¹⁰:

$$\chi_1 = \sum_2 H_{12} v_2, \quad (5)$$

where

$$\chi_1 = -(\hbar \omega_1 / T^2) \vec{v}_1 \cdot \vec{\nabla}T / \sinh \frac{1}{2} \beta \hbar \omega_1, \quad (6)$$

with \vec{v}_1 the phonon group velocity $\vec{\nabla}_{\vec{q}_1} \omega_{\vec{q}_1 s_1}$; the deviation from equilibrium is now described by

$$v_1 = n_1 \sinh \left(\frac{1}{2} \beta \hbar \omega_1 \right), \quad (7)$$

and the symmetric collision operator H is the sum of N - and U -process parts from 3-phonon interactions,¹⁰ plus contributions from "impurity" (including defect) and boundary scattering,

$$H = H^N + H^U + H^I + H^B \equiv H^N + H^R. \quad (8)$$

In the notation of (5)–(7), the diagonal elements of $H/4k$ are the single-mode inverse relaxation times. The thermal conductivity K is¹⁰

$$K = \frac{\mathcal{K}}{V(\vec{\nabla}T/T)^2}, \quad (9)$$

where V is the crystal volume, and the "reduced" thermal conductivity

$$\mathcal{K} = \sum_1 \chi_1 v_1 \equiv \langle \chi | v \rangle. \quad (10)$$

In the variational procedure,^{1,10} one discovers or invents a trial phonon distribution function $u_{\vec{q}s}$ approximating the exact solution $v_{\vec{q}s}$ of the Boltzmann equation (5). The functional

$$\mathcal{K}^{\langle u \rangle} \equiv \frac{\langle \chi | u \rangle^2}{\langle u | H | u \rangle} \quad (11)$$

then gives a lower bound on \mathcal{K} .

If for every phonon, umklapp and other resistive collision processes really are slow in comparison with normal processes, the phonon distribution will

be rapidly driven by the N processes toward a displaced, or drifting, Planck distribution:

$$N_{\vec{q}s} = [\exp(\beta \hbar \omega_{\vec{q}s} - \beta \hbar \vec{q} \cdot \vec{c}) - 1]^{-1},$$

so the deviation from equilibrium is

$$n_{\vec{q}s} \approx \hbar \vec{q} \cdot \vec{c} / 4kT \sinh^2 \left(\frac{1}{2} \beta \hbar \omega_{\vec{q}s} \right). \quad (12)$$

This displaced Planck distribution represents phonon convection; the phonons are in equilibrium in a reference frame moving with velocity \vec{c} relative to the lattice.¹¹ Resistive processes tend to slowly reduce the convection velocity to zero, while an applied temperature gradient counteracts this tendency; in the steady state one would thus expect $\vec{c} \propto -\vec{\nabla}T$, and via (7) a trial function $|u^D\rangle$ corresponding to a displaced Planck distribution is then

$$u_{\vec{q}s}^D = -\nabla T \cdot \frac{\hbar \vec{q}}{4kT \sinh \left(\frac{1}{2} \beta \hbar \omega_{\vec{q}s} \right)} \equiv -\vec{\nabla}T \cdot \vec{\mu}_{\vec{q}s}. \quad (13)$$

Substituted into (11), this trial function gives the thermal conductivity in the Ziman limit, $K_Z^{\langle \rangle}$, which, using (6) and (9), can be put in the form

$$K_Z^{\langle \rangle} = C_0 v_{\text{II}}^2 \tau_Z^R. \quad (14)$$

Here C_0 is the heat capacity per unit volume,

$$C_0 = V^{-1} \sum_{\vec{q}s} C_{\vec{q}s},$$

with

$$C_{\vec{q}s} = (\hbar \omega_{\vec{q}s})^2 / 4kT^2 \sinh^2 \left(\frac{1}{2} \beta \hbar \omega_{\vec{q}s} \right), \quad (15)$$

v_{II} is the velocity of drifting second sound,

$$v_{\text{II}}^2 = \frac{(\sum_{\vec{q}s} C_{\vec{q}s} \vec{q} \cdot \vec{v}_{\vec{q}s} / \omega_{\vec{q}s})^2}{3VC_0 \sum_{\vec{q}s} C_{\vec{q}s} \omega_{\vec{q}s}^2 / \omega_{\vec{q}s}^2}, \quad (16)$$

and the Ziman-limit relaxation time τ_Z^R is given by

$$1/\tau_Z^R = \sum_{1,2} \vec{\mu}_1 \cdot H_{12}^R \vec{\mu}_2 / 4k \sum_1 \vec{\mu}_1 \cdot \vec{\mu}_1, \quad (17)$$

with $\vec{\mu}_1 \equiv \vec{\mu}_{\vec{q}_1 s_1}$ as in (13) above. The Ziman limit (14)–(17) has been obtained in several ways,^{1,2,4,12} the essential ingredient always being physical intuition to motivate the displaced Planck distribution.

However, one should not expect the displaced Planck function to adequately represent the steady-state distribution of high-energy phonons. Because τ^N and τ^U are comparable for these phonons, they should not be expected to drift at the same rate as the low-energy "thermal" phonons, but should be more nearly in equilibrium. Thus we propose the following modification of the displaced Planck function (13):

$$u_{\vec{q}s}^D = u_{\vec{q}s}^D [1 - a \Theta(\omega_{\vec{q}s} - \omega_l^{\text{min}}) \delta_{s,l}]. \quad (18)$$

Here a is a variational parameter and Θ the Heaviside step function. Longitudinal phonons with $\omega \geq \omega_l^{\text{min}}$, the minimum frequency for the onset of the umklapp process $l \rightarrow (2 \text{ other phonons})$, drift at a

slower rate than all the other phonons, if a comes out between 0 and 1. In principle one should also include a similar modification for the fast transverse branch near the zone boundaries, since such phonons can also undergo spontaneous emission decay processes of the type envisaged in Sec. II, but such refinements will be ignored.

The variational parameter a is chosen by putting the function (18) into the bound (11) and maximizing the resulting $\mathcal{K}^{\langle} (u)$ with respect to a . If we abbreviate (18) as

$$|u\rangle = |u^D\rangle - a|w\rangle,$$

the result is

$$a = \frac{\langle \chi | u^D \rangle \langle u^D | H | w \rangle - \langle \chi | w \rangle \langle u^D | H | u^D \rangle}{\langle \chi | u^D \rangle \langle w | H | w \rangle - \langle \chi | w \rangle \langle u^D | H | w \rangle}. \quad (19)$$

Henceforth we denote by \mathcal{K}^{\langle} the value of (11) computed using (18) with this optimum value of a . It is this quantity whose computation is described in Sec. IV.

An approximate form of the bound \mathcal{K}^{\langle} , while not crucial, seems instructive. At temperatures such that $kT \ll \hbar\omega_1^{\text{min}}$, the terms in (19) involving the factor $\langle \chi | w \rangle$ will be small, so that

$$a \approx \frac{\langle u^D | H | w \rangle}{\langle w | H | w \rangle}.$$

Similarly the numerator in the expression (11) for \mathcal{K}^{\langle} is also approximately $\langle \chi | u^D \rangle^2$. In addition the single-mode relaxation-time approximation of H should be valid⁸ for energies $\hbar\omega \gg kT$, so if we also replace H^N and H^R by their diagonal elements $4k/\tau_{\vec{q}s}^N$ and $4k/\tau_{\vec{q}s}^R$ everywhere a matrix element involving $|w\rangle$ occurs, then \mathcal{K}^{\langle} can be put in a form similar to (14):

$$\begin{aligned} K^{\langle} &= C_0 v_{\text{IT}}^2 \tau; \\ \frac{1}{\tau} &= \frac{1}{\tau_Z^{\langle}} - \frac{\langle 1/\tau^R \rangle_{\text{ht}}^2}{\langle 1/\tau^R + 1/\tau^N \rangle_{\text{ht}}}. \end{aligned} \quad (20)$$

The high-frequency average in (20) is defined by

$$\langle \tau^{-1} \rangle_{\text{ht}} = \frac{\sum_{\text{ht}} \tau_{\vec{q}s}^{-1} C_{\vec{q}s} q^2 / \omega_{\vec{q}s}^2}{\sum C_{\vec{q}s} q^2 / \omega_{\vec{q}s}^2}.$$

The sum in the numerator is only over longitudinal modes with $\omega \geq \omega_1^{\text{min}}$. The form (20) is particularly suggestive—it makes it clear that if there are a large enough number of high-energy modes with $\tau^U \approx \tau^N$ to make a significant contribution to $1/\tau_Z^{\langle}$, then the thermal conductivity lifetime τ is greater than τ_Z^{\langle} , and the Ziman limit will never be approached.

IV. MODEL CALCULATION

Computation of the bounds \mathcal{K}^{\langle} and \mathcal{K}_Z^{\langle} of Sec. III was performed using the simplified isotropic dispersionless lattice model proposed by Hamilton and Parrott,¹³ with a few minor exceptions. We give

details below.

Harmonic Phonons

The phonon spectrum contains two degenerate transverse branches with frequencies

$$\omega_{\vec{q}t} = c_t q,$$

and a longitudinal branch with frequencies

$$\omega_{\vec{q}l} = c_l q.$$

The sound-velocity ratio is chosen to be that appropriate for polycrystals of a classical cubic solid with elastic constants satisfying $C_{12} = C_{44} = \frac{1}{2}C_{11}$, namely,

$$c_l/c_t = r = 1.76.$$

The first Brillouin zone is replaced by a Debye sphere, radius q_D , of the same volume. Thus in applying the model to alkali halides we omit optical phonons.

Debye temperatures Θ_s for the two branches are defined by

$$k\Theta_s = \hbar c_s q_D, \quad (21)$$

where s stands for either l or t . In applying the calculations to experiment, Θ_t (or equivalently Θ_t , since c_l/c_t is fixed) is used as an adjustable parameter to fit the conductivity data. This has the effect of matching the model dispersionless phonon spectrum to the real spectrum at the high-frequency end, rather than at the low-frequency end, since the actual conductivity in the umklapp region reflects phonon frequencies fairly near the zone boundaries.

Anharmonic Interactions

We take the cubic anharmonic coefficients to be¹⁴

$$|\Phi_{123}|^2 = (0.0474 \hbar^3 \gamma^2 / N m c_t^2) \omega_1 \omega_2 \omega_3 \Delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3),$$

where N is the number of primitive unit cells in the crystal, m is the mass per unit cell, Δ is the lattice Kronecker Δ function, and the Grüneisen constant γ is treated as an adjustable parameter to fit conductivity data. The device of Hamilton and Parrott¹³ is used to include umklapp processes: for the umklapp process $(\vec{q}_1 s_1) + (\vec{q}_2 s_2) \rightleftharpoons (-\vec{q}_3 s_3)$, the only allowed value for the reciprocal lattice vector $\vec{G} = \vec{q}_1 + \vec{q}_2 + \vec{q}_3$ is defined to be the vector of magnitude $2q_D$ directed along $\vec{q}_1 + \vec{q}_2$. The allowed three-phonon processes for this model and their regions of phase space are discussed in Ref. 13. One has

(a) $t_1 + l_2 \rightleftharpoons l_3$, both normal and umklapp, is allowed. The U process requires $\omega_3 \geq \omega_3^{\text{min}} = [(r+1)/2r]c_l q_D$, or $q_3 \geq 0.785q_D$ here.

(b) $t_1 + t_2 \rightleftharpoons l_3$, both N and U , is allowed. The U process requires $\omega_3 \geq \omega_3^{\text{min}} = [2/(r+1)]c_l q_D$, or $q_3 \geq 0.725q_D$ here.

(c) $l_1 + l_2 \rightleftharpoons l_3$ and $t_1 + t_2 \rightleftharpoons t_3$ N processes are also

allowed for all three wave vectors collinear. Since these processes become forbidden when dispersion is added to the phonon spectrum, we have simply ignored them.

The $t+t \Rightarrow l$ process was found to dominate the low-temperature thermal resistance. This is expected for two reasons: First and foremost, it can attenuate a transverse thermal phonon at less expense of energy, since ω_3^{min} is smaller for this process; and second, it has large phase space in the vicinity of q_3^{min} .

Numerical Computations

If for the moment we neglect impurity and boundary scattering, then evaluation of $\mathcal{K}^<$ and $\mathcal{K}_Z^<$ requires computation of the four matrix elements

$$\langle u^D | H^U | u^D \rangle, \quad \langle u^D | H^U | w \rangle, \\ \langle w | H^N | w \rangle, \quad \langle w | H^U | w \rangle.$$

Each matrix element is the sum of contributions from the two three-phonon processes above. The simplicity of the model used permits analytic solution of the energy and quasimomentum conservation laws to identify the allowed regions of phase space for each process. Each matrix element then reduces to evaluation of two two-dimensional integrals, which has been carried out numerically at several values of T/Θ_t . Selected results are shown in Table I. The variational parameter a is never

TABLE I. Variational parameter a and conductivity ratio as functions of temperature. $K_Z^<$ is the conductivity in the Ziman limit ($a \equiv 0$).

T/Θ_t	a	$K^</K_Z^<$
$\frac{1}{20}$	0.827	1.46
$\frac{1}{18}$	0.829	1.47
$\frac{1}{16}$	0.831	1.48
$\frac{1}{15}$	0.834	1.48
$\frac{1}{14}$	0.836	1.49
$\frac{1}{13}$	0.838	1.50
$\frac{1}{12}$	0.839	1.50
$\frac{1}{10}$	0.847	1.53
$\frac{1}{8}$	0.845	1.54
$\frac{1}{6}$	0.844	1.55
$\frac{1}{4}$	0.786	1.46
$\frac{1}{2}$	0.650	1.28
1	0.566	1.20
2	0.538	1.17
10	0.528	1.17

small. Its low-temperature value of about 0.83 means that high-frequency longitudinal phonons with $q \geq 0.725 q_D$ drift at only 17% of the drift velocity of the rest of the distribution. This very substantial change accounts for the conductivity $\mathcal{K}^<$ being about 50% higher than the Ziman limit and never approaching it at any temperature. Thus about $\frac{1}{3}$ of the thermal conductivity of this model comes explicitly from normal processes. The computed numbers in Table I depend only on the chosen value of c_l/c_t ; they are independent of what values one chooses for the Grüneisen constant and the Debye temperature.

V. APPLICATION TO LiF AND NaF

Since the main interest in this work is on the treatment of intrinsic scattering processes, we shall simply treat all impurities as if they scattered phonons like point-mass defects. This should not be too unreasonable an approximation for foreign alkali atoms, which appear to be the main defects in the experiments considered.

Point-Defect Scattering

Point-defect scattering of phonons is exactly characterized by a relaxation time¹⁵; the contribution to the collision operator is thus diagonal:

$$H_{\vec{q}s, \vec{q}'s'}^I = \Delta(\vec{q} - \vec{q}') \delta_{ss'} 4k/\tau_{\vec{q}s}^I,$$

where¹⁶

$$1/\tau_{\vec{q}s}^I = (\Omega_0 \Gamma / 4\pi v^3) \omega_{\vec{q}s}^4,$$

with Ω_0 the volume of the primitive unit cell and

$$v^{-3} = \frac{1}{3}(c_l^{-3} + 2c_t^{-3}).$$

Γ , which characterizes the concentration and scattering strength of the defects,¹⁶ is treated as an adjustable parameter.

Boundary Scattering

To simulate phonon scattering from the boundaries of a finite crystal, we add a constant diagonal term H^B to the collision operator:

$$H_{\vec{q}s, \vec{q}'s'}^B = 4k(c_s/L) \Delta(\vec{q} - \vec{q}') \delta_{ss'}.$$

Simons,¹⁷ Ziman,¹⁸ and Carruthers¹⁶ have discussed the adequacy of this approximation. The parameter L is the Casimir length¹⁹ of the crystal. For the LiF and NaF experiments this length can be estimated independently, but instead we treat L as an adjustable parameter to compensate for the fact that the sound velocities of the model do not accurately represent the phonon frequency spectrum at long wavelengths, where boundary scattering is important—see the discussion following Eq. (21).

In both cases to be treated the addition of enough boundary and isotope scattering to fit the data makes negligible change in the variational parameter a ,

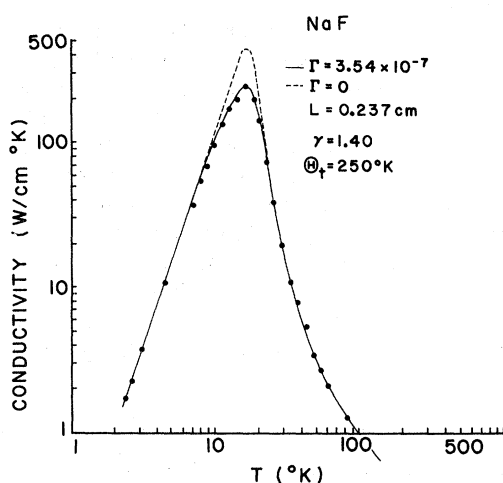


FIG. 1. Thermal conductivity of NaF. Circles: Jackson and Walker, Ref. 6. Lines: this work, with adjusted parameters as shown. See text, Sec. V.

which remains that determined in Table I from anharmonic scattering. Boundaries and defects scatter high-frequency phonons very weakly in comparison with intrinsic spontaneous emission processes.

NaF

Figure 1 displays the results of adjusting model parameters to fit the measurements of Jackson and Walker⁶ on ultrapure NaF. The dashed higher curve shows the thermal conductivity of a fictitious crystal with no isotopic impurities. The difference at the peak between the dashed and solid curves is thus all attributed to isotope scattering; $\Gamma = 3.54 \times 10^{-7}$ corresponds to a total of 2.3 ppm of Ca^{++} and/or K^+ defects. This is perhaps too high a concentration. Jackson and Walker indicate that the chemical impurity content of their crystal was about 1 ppm, so that some of what here masquerades as isotope scattering should really be attributed to dislocations. The excellence of the fit shown in Fig. 1, however, indicates that such a separation would have to be arbitrary.

The adjusted value of 1.40 for the Grüneisen constant seems quite reasonable (the smoothed experimental value²⁰ is 1.53). The adjusted Θ_T of 440 °K (1.76 times Θ_T) is slightly less than $\Theta_D = 466$ °K from the low-temperature heat capacity. One expects this; the maximum acoustic frequency should be somewhat less than Θ_D because of dispersion in the phonon spectrum at high frequencies. Thus two adjustable parameters appear sufficient to fit the anharmonic contribution to the conductivity at all temperatures, whereas a Callaway-model analysis requires five.⁶

Regardless of the ambiguity in treating the defect scattering, it is clear from Fig. 1 that 25 °K

($T/\Theta_T = \frac{1}{10}$, $T/\Theta_D \approx \frac{1}{19}$) represents a temperature at which the conductivity is very far into the umklapp region, with the resistance from defects still negligible. If the Ziman limit is valid at all it should thus be so at 25 °K, yet Table I shows that it underestimates the conductivity by more than 50% in this temperature range.

LiF

In Fig. 2 we show the result of fitting model parameters to the conductivity of Li^7F measured by Thacher.²¹ As before, the dashed curve shows the conductivity of a hypothetical perfect crystal of the same size. The chemical purity of Thacher's crystal is not known. One component is identifiable: the crystal did contain 100 ppm of Li^6 defects, but the adjusted $\Gamma = 2.55 \times 10^{-6}$ corresponds to 1600 ppm Li^6 . In fact the slight discrepancy between fit and experiment around the peak indicates that the chemical impurities do not act purely as mass defects. Inclusion of dislocation scattering would if anything strengthen this conclusion, since it would accentuate rather than reduce the asymmetry between the theoretical and experimental curves near the peak.

The adjusted Grüneisen constant $\gamma = 2.086$ is somewhat higher than the experimental value,²² which between 0 °K and room temperature always lies between 1.6 and 1.7. The adjusted Θ_T of 650 °K is again reasonable; the specific heat Θ_D is 720 °K.

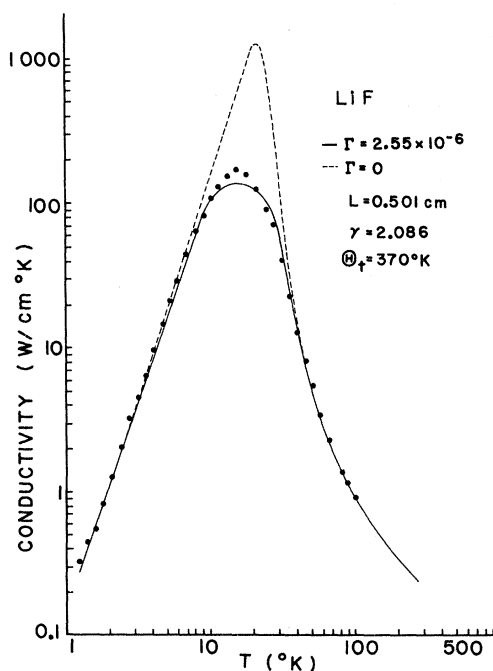


FIG. 2. Thermal conductivity of LiF. Circles: Thacher, Ref. 21. Lines: this work, with adjusted parameters as shown. See text, Sec. V.

As with NaF, the thermal resistance is dominated by intrinsic processes to temperatures as low as $\frac{1}{10}\Theta_D$ or $\frac{1}{19}\Theta_D$.

Thacher's data on LiF have also been analyzed by Guyer and Sarkissian.²³

VI. CONCLUSION

Of course there is no *direct* experimental evidence that the Ziman limit is not (or is) achieved, but this analysis shows that if the model is realistic then the effect of spontaneous-emission umklapp processes envisioned in Sec. III really is reflected

in the experimental conductivities. A simpler but less controlled test would be to use the relaxation-time approximation directly in Eqs. (17) and (20); however, care must be taken to use reasonable relaxation time forms for high as well as low frequencies.

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