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Solving the phonon Boltzmann equation with the variational method

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The thermal conductivity of 17 alkali halides with the NaCl structure has been calculated. The deformation-dipole model has been used to calculate realistic phonon dispersion relations, which are used to solve the Boltzmann equation with the variational method. Many different trial functions and linear combinations have been used and the resultant approximate solutions are discussed. Assuming different trial functions for different branches increases the calculated thermal conductivity by 10–150 % . The error estimates suggest that the true solution to the Boltzmann equation would increase the calculated thermal conductivity by another 100% .

I. INTRODUCTION

The phonon Boltzmann equation was first derived by Peierls.[1] It can be written as

$$\dot{N}_{\mathrm{drift}}(\mathbf{q},j) + \dot{N}_{\mathrm{scatt}}(\mathbf{q},j) = 0, \tag{1}$$

where $\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$ is the rate of change of the number of phonons with wave vector $\mathbf{q}$ and branch index j due to the temperature gradient $\boldsymbol{\nabla}T$, and $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$ is the rate of change due to scattering of the phonon against boundaries, impurities, dislocations, electrons, or other phonons. This paper discusses the Boltzmann equation for alkali halide crystals at high temperatures. The alkali halides are insulators and it is only the three-phonon scattering processes that need to be considered at high temperatures. It is convenient to write the deviation $n(\mathbf{q},j)$ from the thermal equilibrium distribution $N_0(\mathbf{q},j)$ as

$$\begin{aligned} n(\mathbf{q},j) &\equiv N(\mathbf{q},j) - N_0(\mathbf{q},j) \\ &= \frac{N_0(\mathbf{q},j)[N_0(\mathbf{q},j)+1]}{kT} g(\mathbf{q},j), \end{aligned} \tag{2}$$

where k is the Boltzmann constant. The two terms in Eq. (1) can now be written as

$$\dot{N}_{\mathrm{drift}}(\mathbf{q},j) = \frac{-\hbar\omega(\mathbf{q},j)}{kT^2} N_0(\mathbf{q},j)[N_0(\mathbf{q},j)+1]\mathbf{v}(\mathbf{q},j)\cdot\boldsymbol{\nabla}T, \tag{3}$$

$$\begin{aligned} \dot{N}_{\mathrm{scatt}}(\mathbf{q},j) = \frac{\pi}{kT\hbar^2} \sum_{\mathbf{q}'j',\mathbf{q}''j''} |\Phi^{jj'j''}_{\mathbf{q}\mathbf{q}'\mathbf{q}''}|^2 \{ & \delta(\omega(\mathbf{q},j) - \omega(\mathbf{q}',j') - \omega(\mathbf{q}'',j''))(N_0+1)N_0'N_0'' \\ & \times[g(-\mathbf{q}',j') + g(-\mathbf{q}'',j'') - g(\mathbf{q},j)] \\ & +2\delta(\omega(\mathbf{q},j) + \omega(\mathbf{q}',j') - \omega(\mathbf{q}'',j''))(N_0+1)(N_0'+1)N_0'' \end{aligned} \tag{4}$$

where $|\Phi^{jj'j''}_{\mathbf{q}\mathbf{q}'\mathbf{q}''}|^2$ stands for a lengthy expression involving eigenvectors, frequencies, and a third-order derivative of the potential energy C_{111}. The exact expression is given in Refs. 2 and 3.

There have been many attempts to solve the Boltzmann equation through approximate methods. Two widely used approaches are the relaxation-time method[4] and the Callaway theory.[5] The phonon dispersion relations have been approximated by a Debye model in most cases but there are a few calculations[6,7] that are based on realistic dispersion relations.

Another well-known method is the variational method which will be used in this paper. One starts by assuming some relationship between g and $\mathbf{q}, j$. This means that the exact solution g is replaced by a trial function f. According to the variational principle, the best solution to the Boltzmann equation makes the thermal conductivity a maximum.

The most popular choice of the trial function f has been

$$f_1 = A_1 \nabla T \cdot \mathbf{q}, \tag{5}$$

where A_1 is a constant to be determined. This choice of trial function was expected to give a high value of the thermal conductivity since the normal processes do not contribute to the thermal resistivity in this case. This is the basis for the famous Leibfried-Schlömann formula[8] which has later been modified in order to include optic branches.[9] Julian[10] used realistic dispersion relations and the above trial function in calculations of the thermal conductivity of rare-gas crystals. Although Julian used another formalism to solve the Boltzmann equation, his final expression is equivalent to what is obtained with the variational method.

In a series of previous papers,[2,11,12] the thermal conductivity of alkali halide crystals with the NaCl structure was calculated. The phonon dispersion relations were calculated with a deformation-dipole model with low-temperature values of the input parameters and the variational method was used to obtain the thermal conductivity. It was found[2] that another choice of trial function,

$$f_2 = A_2 \nabla T \cdot \mathbf{v}(\mathbf{q}, j), \tag{6}$$

where $\mathbf{v}$ is the group velocity of the phonon, gave values for the thermal conductivity that were 5–10 times higher than the values obtained with f_1 at high temperatures. With this trial function f_2, the calculated thermal-conductivity values were no more than 15–20 % lower than the experimental values, in most cases. The trial function f_2 has been found to be better than f_1 also in the case of rare-gas crystals.[13]

One might think that the good agreement between theory and experiment would imply that f_2 is a very good trial function but one must keep in mind that there are great uncertainties in other parts of the calculations as well. Following the discussion and the estimates that are given in Ref. 2, terms in the phonon scattering operator that are assumed to be unimportant have been neglected. One of the greatest uncertainties is in the value assigned for a third-order derivative of the potential energy.[2] It is quite possible that better trial functions would give thermal-conductivity values that are much higher than the experimental values. This in turn would imply that other parts of the theory have to be improved since the variational method always gives a lower limit to the thermal conductivity of the model crystal.

This paper examines some other possible trial functions and linear combinations of these. The new trial functions are obtained by dividing f_2 by some power of the phonon frequency. The reason for this choice will be explained below. Linear combinations of trial functions have been used before,[14,15] but they have been based on the trial function f_1 and the complicated integrals involved have been evaluated through crude approximations in which optic phonons have been neglected. It is interesting to note that Benin[15] found that phonons close to the Brillouin-zone boundary should be closer to thermal equilibrium than the phonons in the center of the zone. This is automatically fulfilled when f_2 is used as the trial function.

In a previous paper,[11] the relative importance of the optic branches was discussed. Since there was only one parameter to vary, their relative contribution was, in some sense, determined as soon as the choice of trial function was made. The theoretical calculations will now be improved by assuming different trial functions for the acoustic and optic branches, respectively, which makes it possible to test the previous conclusions about the role of optic phonons. A preliminary report of part of this work was given in Ref. 16.

II. THEORY

A variational method will be used to solve the linearized Boltzmann equation

$$\theta = \hat{G} g, \tag{7}$$

where θ is the drift term in Eq. (1) and $\hat{G}g$ is equal to $-\dot{N}_{\text{scatt}}(\mathbf{q}, j)$. It is convenient to define an inner product by

$$(s(\mathbf{q}), t(\mathbf{q})) = \sum_{\mathbf{q}} s(\mathbf{q}) t(\mathbf{q}). \tag{8}$$

The variational principle states that of all functions f that satisfy

$$(f, \theta) = (f, \hat{G} f) \tag{9}$$

the exact solution to Eq. (7), $f = g$, is the function that gives (f, θ) or $(f, \hat{G} f)$ its maximum value. This implies that the exact solution to Eq.(7) makes the thermal conductivity λ a maximum, since λ is proportional to (g, θ).

In the previous calculations,[2,11,12] a trial function was used whose only constant [see Eq. (6)] was determined already by the constraint in Eq. (9). In the present calculations, linear combinations of trial functions,

$$f = \sum_i C_i f_i \tag{10}$$

have been used, where the functions f_i will be described in the next section.

The problem of finding the maximum of (f,θ), subject to the constraint in Eq. (9), is easily solved by the method of Lagrange multipliers. In this case it can be shown that the Lagrange multiplier is equal to -1 and the problem is reduced to solving a system of linear equations,

$$\theta_i = \sum_l C_l G_{il}, \tag{11}$$

where

$$\theta_i = (f_i,\theta) = \sum_{\mathbf{q}j} \frac{-\hbar\omega(\mathbf{q},j)}{kT^2} f_i(\mathbf{q},j) N_0(\mathbf{q},j)[N_0(\mathbf{q},j)+1]\mathbf{v}(\mathbf{q},j)\cdot\boldsymbol{\nabla}T \tag{12}$$

and

$$\begin{aligned} G_{il} &= (f_i,\hat{G}f_l) \\ &= \frac{\pi}{kT\hbar^2} \sum_{\mathbf{q}j,\mathbf{q}'j',\mathbf{q}''j''} |\Phi^{jj'j''}_{\mathbf{q}\mathbf{q}'\mathbf{q}''}|^2 \delta(\omega(\mathbf{q},j)-\omega(\mathbf{q}',j')-\omega(\mathbf{q}'',j''))[N_0(\mathbf{q},j)+1]N_0(\mathbf{q}',j')N_0(\mathbf{q}'',j'') \\ &\qquad \times [f_i(-\mathbf{q},j)-f_i(\mathbf{q}',j')-f_i(\mathbf{q}'',j'')][f_l(-\mathbf{q},j)-f_l(\mathbf{q}',j')-f_l(\mathbf{q}'',j'')]. \end{aligned} \tag{13}$$

It is clear that G_{il} is symmetric in $\mathbf{q}'',j''$ and $\mathbf{q}',j'$ and it is therefore possible to restrict the sums to $|\mathbf{q}''| > |\mathbf{q}'|$ and multiply the result by 2. More information on how to evaluate integrals like θ_i and G_{il} is given in Refs. 2 and 3.

III. TRIAL FUNCTIONS

The acoustic-phonon branches tend to zero frequency as $|\mathbf{q}|$ goes to zero while the optic branches have a large frequency for all values of $\mathbf{q}$. It is therefore plausible that the phonon distribution will be very different for these two groups of phonons. In this paper, linear combinations of trial functions will be used, where each individual trial function is describing either optic phonons or acoustic phonons.

A set of "optic trial functions" is defined by

$$f_{Om}(\mathbf{q},j) = \begin{cases} 0 \quad \text{if } j = 1,\ 2, \text{or } 3 \\ \qquad\qquad (\text{acoustic branches}) \\ \dfrac{\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)}{\omega^m(\mathbf{q},j)} \quad \text{if } j = 4,\ 5, \text{or } 6 \\ \qquad\qquad (\text{optic branches}), \end{cases} \tag{14}$$

for $m = 0,\ 1,\ 2,\ 3,\ 4,$ or 5, where ω is the phonon frequency. "Acoustic trial functions" are defined in the same way:

$$f_{A0}(\mathbf{q},j) = \begin{cases} \dfrac{\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)}{\omega^n(\mathbf{q},j)} \quad \text{if } j = 1,\ 2, \text{or } 3 \\ \qquad\qquad (\text{acoustic branches}) \\ 0 \quad \text{if } j = 4,\ 5, \text{or } 6 \\ \qquad\qquad (\text{optic branches}) \end{cases} \tag{15}$$

for $n = 0$. In the case of the "acoustic trial funtions," n cannot be allowed to be larger than 0 since the θ_i and G_{il} integrals would not converge. In a preliminary report,[16] an acoustic trial function with $n = 1$ was also used, but due to normal processes, such a choice would make the integral $(f,\hat{G}f)$ diverge. This divergence does not show up in the numerical calculations since the integrals are approximated as a sum over $\mathbf{q}$ vectors distributed on a regular mesh.

The factor $\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)$ is included in all trial functions since this will always give a positive relaxation time when there is only one trial function. It can be shown that the relaxation time $\tau(\mathbf{q},j)$ in this case is given by

$$\begin{aligned} \tau(\mathbf{q},j) &= \frac{-T}{\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)\hbar\omega(\mathbf{q},j)} C_n f_n(\mathbf{q},j) \\ &= \frac{-T}{\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)\hbar\omega(\mathbf{q},j)} \frac{C_n \boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)}{\omega^n(\mathbf{q},j)}, \end{aligned} \tag{16}$$

where the constant C_n is negative. If $\boldsymbol{\nabla}T\cdot\mathbf{q}$ instead of $\boldsymbol{\nabla}T\cdot\mathbf{v}(\mathbf{q},j)$ had been included in the definition of the trial function it would have resulted in negative relaxation times for those phonons where $\mathbf{q}$ and $\mathbf{v}(\mathbf{q},j)$ point in opposite directions.

When linear combinations of the trial functions are used, it is possible that the solution corresponds to negative relaxation times for some phonons, since the solution is a sum over the trial functions with their associated constants C_n. Some of these constants are positive while others are negative. The results that will be presented in the next section do show that the solutions in some cases correspond to negative relaxation times for a small number of phonons. A phonon with a negative relaxation time would make a negative contribution to the thermal conductivity, i.e., it would effectively carry heat in the wrong direction.

The trial functions are chosen so that they are identical except for the frequency dependence. There have been several suggestions for the frequency dependence of the relaxation time $\tau \propto [\omega(\mathbf{q},j)]^{-n-1}$, with n ranging from 0 to 4.[4,17–20] Often n is assumed to be equal to 1 due to umklapp processes. The value n=4 has been used only for high-frequency longitudinal-acoustic phonons.

IV. RESULT OF CALCULATIONS

Results will be given only for $T = 300$ K. A discussion of the temperature dependence is found in a preliminary report.[16] The calculated thermal conductivity at 300 K is given in Table I for different trial functions. Values that were obtained with the trial functions f_1 and f_2 in previous calculations have also been included. The values listed in columns 3 and 4 of Table I differ in three cases (LiBr, LiI, and RbI) from those reported in Ref. 2. The values reported previously for RbI are not correct. Next-nearest-neighbor short-range interactions between negative ions have been included in this work in the calculation of the dispersion relations for LiBr and LiI. This gives a better fit of the infrared dispersion frequency and changes the dispersion relation for the optic branches considerably. The calculated thermal conductivity also changes significantly.

A. Two trial functions

The first discussion will be on linear combinations of one "acoustic trial function" and one "optic trial function." The object is to see how important it is to assume different trial functions for the acoustic and optic branches and also to determine the frequency dependence for the optic phonons that corresponds to the best solution to the Boltzmann equation.

The thermal conductivity λ was calculated for all 17 alkali halide crystals with m equal to 0 or 1 in Eq. (14) and it was found that at high temperatures $m = 1$ is better than $m = 0$ in 15 of the crystals. It is only for LiBr and LiI that $m = 0$ is better. In Table I the results for $m = 1$ are given. When compared to the results obtained with the previous best trial function, f_2, the thermal conductivity increases by 2–14 % for crystals where the ratio of the ion masses is less than 3. The increase in the thermal conductivity is considerably larger for crystals with a mass ratio larger than 3. The extreme case is CsF where λ increases by 150%.

It has been estimated[17,18] that the relaxation time for high-frequency phonons should be proportional to ω^{-2} which corresponds to m=1. Optic trial functions with m ranging all the way from m=0 to 5 were used in six crystals. It was found in these cases that the highest λ values were found for m= 2 and 3, except in NaI where it was found for m=5. The thermal conductivity does not seem to be very sensitive to the choice of the optic trial function.

One of the reasons for assuming different trial functions for the acoustic and optic branches, respectively, was to let the relative importance of acoustic versus optic branches be determined by the variational principle. The optic phonons carry approximately 30% of the heat in NaF, KCl, and RbBr where the two different ions have almost the same masses. They carry a smaller portion

TABLE I. The thermal conductivity λ_i at 300 K of 17 alkali halides calculated with different linear combinations of trial functions f_i that are given in Eqs. (5), (6), (15), and (14). The experimental thermal conductivity λ_{expt} has been corrected to constant volume, corresponding to the volume at T=0 K. C_{111} is a third-order derivative of the potential energy. Units: λ (W m^{-1} K^{-1}), C_{111} (10^{12} Pa).

Crystal	C_{111}	λ_1	λ_2	$\lambda_{A0,O1}$	$\lambda_{A0,O1,O2}$	λ_{expt}	Ref.
LiF	−1.194	2.78	14.2	16.2	16.2	16.1	Ref. 21
LiCl	−0.766	0.385	2.48	5.17	5.19		
LiBr	−0.486	0.261	1.57	3.15	3.25	2.20	Ref. 22
LiI	−0.252	0.349	2.08	3.39	3.75		
NaF	−1.220	4.80	20.9	22.7	25.5	18.5	Ref. 23
NaCl	−0.718	1.06	6.34	6.63	7.00	7.20	Ref. 24
NaBr	−0.650	0.252	2.51	3.04	3.08	2.86	Ref. 25
NaI	−0.559	0.129	1.42	2.56	2.65	1.91	Ref. 24
KF	−1.013	1.17	5.79	6.47	6.96	7.81	Ref. 26
KCl	−0.614	0.795	6.45	7.22	7.59	7.20	Ref. 27
KBr	−0.593	0.233	2.60	2.64	2.66	3.43	Ref. 27
KI	−0.404	0.105	1.38	1.55	1.56	2.79	Ref. 27
RbF	−0.871	0.144	1.26	2.12	2.13	2.87	Ref. 22
RbCl	−0.721	0.286	2.59	2.65	2.70	2.89	Ref. 27
RbBr	−0.582	0.285	3.87	4.35	4.48	3.91	Ref. 27
RbI	−0.495	0.160	2.17	2.21	2.23	2.35	Ref. 27
CsF	−0.938	0.0709	0.812	2.06	2.06		

of the heat in the other crystals with the extreme case being CsF where only 2% of the heat is carried by the optic branches. A complete table can be found in Ref. 16. The previous results, in which a high relative amount of heat was thought to be carried by the optic phonons in the Li salts, have shown a dramatic decrease when separate acoustic and optic trial functions are used. Making linear combinations of trial functions in each group of phonons does not further change the relative amount of heat carried by optic phonons. In RbF and CsF nearly all of the heat is carried by acoustic phonons. It is interesting to note that the five crystals that have the mass ratio R closest to unity are the only crystals where the relative optic-phonon contribution increases when better trial functions are used.

In relaxation-time calculations, optic phonons were found to carry 35% of the heat in NaCl (Ref. 6) and KCl,[7] which should be compared to the present results, 23% and 33%, respectively. The agreement for KCl is surprisingly good.

B. Three trial functions

A linear combination was made of one acoustic and two optic trial functions with m equal to 0 and 1 in Eq. (14). The result of the calculations at 300 K is given in the sixth column in Table I. Increasing the number of trial functions from 2 to 3 results in an increase of the thermal conductivity by 2–12%. Making linear combinations of more than two trial functions does not make any greater change in the thermal conductivity. This does not necessarily mean that the values in Table I are very close to the true thermal conductivity of the model crystals since it is possible that there are other factors besides the frequency dependence that are important to include in the trial functions. For instance, it is possible that additional factors of the group velocity should be included.

Since there is a linear combination of two trial functions for the optic branches, it is not obvious that the solution will correspond to positive relaxation times. It is found that most optic phonons do have a positive relaxation time even when a linear combination of trial functions is used, but at low temperatures it is found that phonons above a certain frequency have a negative relaxation time. These phonons will not affect the thermal conductivity since the temperature is so low that hardly any of these phonons are excited. As the temperature is raised, this limiting frequency starts to increase and is usually higher than the largest phonon frequency at high temperatures.

In NaF, NaCl, NaI, and KF, a few phonons are found in the uppermost branch that have a negative relaxation time even at high temperatures. Also in this case these phonons will not subtract significantly from the thermal conductivity since they occupy only a small region in $\mathbf{q}$ space near the Γ point. Phonons with negative relaxation times are also found in LiBr and LiI, but there they are confined to the lowest optic-phonon branch. These phonons are not important for the thermal conductivity since they have low group velocities.

A negative relaxation time for a phonon mode means that the number of phonons in this mode would not relax towards the equilibrium value when the driving force is switched off. Even though such a situation seems to be unphysical, there are cases where such things could happen. In the present case it is possible that the selection rules for the three-phonon processes would force some phonons away from equilibrium in an initial stage. After a while the relaxation time must become positive so that the whole system could relax to equilibrium. However, the number of phonons with negative relaxation times is expected to be small.

C. Other trial functions

It is possible to further divide the phonons into smaller groups. The acoustic phonons have been divided into three groups: low-frequency acoustic, high-frequency transverse acoustic, and high-frequency longitudinal acoustic. Trial functions defined in analogy with Eq. (14) have been tried for each of these groups. With this division it is possible to test trial functions with n greater than 0 for the high-frequency acoustic phonons without problem of convergence for the integrals.

The high-frequency longitudinal-acoustic phonons were especially interesting to study since it has been found both in theory[19,20] and experiment[28] on other crystals that $\tau \propto \omega^{-5}$ at low temperatures for some of these phonons. This would correspond to n=4 in the trial function.

The study was limited to LiI, NaCl, KI, and RbF. The best trial function for the high-frequency longitudinal branch were found to have a frequency dependence, n=0 or 1. This does not necessarily contradict the previous findings that the relaxation time should be proportional to ω^{-5} for high-frequency longitudinal-acoustic phonons. That theory and experiment dealt with longitudinal phonons that were in the linear part of the dispersion relation while the present group of high-frequency acoustic phonons also includes phonons near the zone boundary where there is large dispersion. It was only for RbF that n=2 was found to be the best trial function for a small temperature region around 40 K.

In a similar way, the optic phonons were divided into transverse and longitudinal. It was found that it was better to use a linear combination of f_{O1} and f_{O0} than to divide the optic phonons into transverse and longitudinal and use only one trial function for each group.

The last set of trial functions that will be discussed consists of one trial function for each branch. The acoustic branches were assigned a trial function of type f_{A0} while the optic trial functions were of type f_{O2}. The frequency dependency for the three optic trial functions were selected with the result of Sec. IV A in mind. This set of six trial functions, f_{br}, was applied to four crystals

TABLE II. The thermal conductivity λ_i at 300 K of four alkali halides calculated with different linear combinations of trial functions f_i that are given in Eqs. (5), (6), (15), and (14). σ is an estimate of the error in the solution of the Boltzmann equation. Units: λ (W m^{-1} K^{-1}).

Crystal		f_1	f_2	$f_{A0,O1}$	$f_{A0,O1,O2}$	f_{br}
NaCl	λ	1.06	6.34	6.63	7.00	7.67
	σ	1.00	0.832	0.809	0.773	0.733
KCl	λ	0.795	6.45	7.22	7.59	8.06
	σ	1.00	0.948	0.891	0.839	0.806
RbI	λ	0.160	2.17	2.21	2.23	2.32
	σ	1.00	0.770	0.752	0.750	0.728
CsF	λ	0.0709	0.812	2.06	2.06	2.27
	σ	1.00	0.905	0.733	0.736	0.740

and the result is given in column 7 in Table II. This trial function gives 4–10% higher values of λ than what was obtained with three trial functions.

V. CONTROL OF THE SOLUTION

It is clear from Table I that the calculated thermal conductivity increases by many percent when linear combinations of trial functions are used. How much can it be expected that the thermal conductivity would increase if it would be possible to find better trial functions? It is easily seen in Eq. (13) that $\hat{G}$ is a symmetric and positive definite operator and a simple derivation shows that

$$(g,\theta) = (f,\theta) + ([g-f],\hat{G}[g-f]). \tag{17}$$

Since λ is proportional to (g,θ), it follows from Eq. (17) that the error in λ is second order in the error in f. However, this is of no help since the exact solution g is not known. The error will instead be estimated by the extent to which the Boltzmann equation, Eq. (1), is fulfilled with the approximate solutions.

The computer code was changed so that it was possible to evaluate Eq. (4) and compare to Eq. (3). The symmetry between $\mathbf{q}'$ and $\mathbf{q}''$ that is present in Eq. (13) is not present in Eq. (4) which makes a greater uncertainty in the numbers that are obtained from the program. The integrals G_{il} are typically 20% greater than when calculated from Eq. (13).

In Figs.1(a)–1(d), Eq. (3) is compared with Eq. (4)

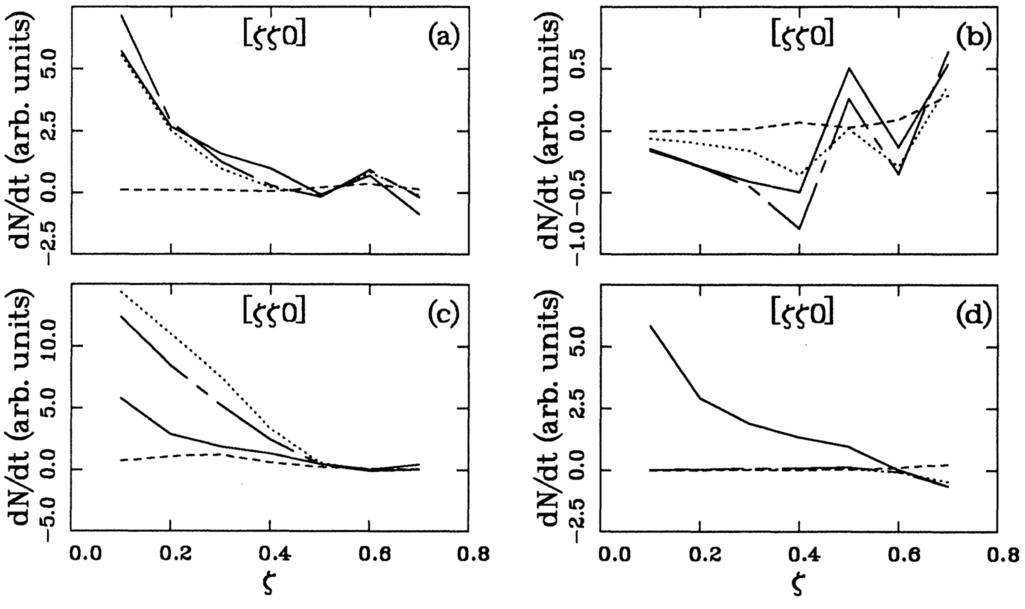

FIG. 1. Comparison of the two terms in Eq. (1) for $\mathbf{q}$ vectors in the [110] direction for different phonon branches in NaCl. $\xi = q/(2\pi/a)$ is the dimensionless reduced-wave-vector coordinate. Solid curve is $-\dot{N}_{\text{drift}}(\mathbf{q},j)$. The other curves are $\dot{N}_{\text{scatt}}(\mathbf{q},j)$ calculated with different trial functions f. The dashed line is obtained from f_1, the dotted line from f_2, and the dot-dashed line is obtained from f_{br}; (a) LA branch; (b) TO_1 branch; (c) TA_2 branch; (d) TA_1 branch.

for $\mathbf{q}$ vectors in the [110] direction for different phonon branches in NaCl. For each wave vector $\mathbf{q}$, the two lowest-lying branches are named transverse acoustic (TA). The next branches are, in order, longitudinal acoustic (LA), tranverse optic (TO), and longitudinal optic (LO). The two terms in Eq. (1) are compared for the longitudinal-acoustic branch in Fig. 1(a). The solid line is $-\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$ and the wiggling behavior at high values of ξ is explained by the way the LA branch is defined. $-\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$ is namely proportional to the group velocity, which changes sign several times in the [110] direction (cf. Fig. 2). The other lines are $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$, where g is replaced with various approximate solutions f. The dashed line is the solution obtained with the trial function f_1 and it is easily seen that there are large differences between the two terms in Eq. (1), especially at small q values. A much better agreement is obtained with the trial functions f_2 and f_{br}, shown with dotted and dotted-dashed lines, respectively. These two solutions have even the correct wiggling behavior at large q vectors.

The result for the TO_1 branch is shown in Fig. 1(b) from which it is clear that the trial function f_{br} works best. An important flaw with the trial function f_1 is also obvious in this figure. $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$ is found to be positive for all $\mathbf{q}$ vectors and does not follow the sign changes that occurs for $-\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$.

In Fig. 1(c) the result for the TA_2 branch is shown. None of the trial functions works well for the TA_2 branch and the situation gets really bad for the TA_1 branch [Fig. 1(d)].

The calculations show that the error is not the same in different directions, which can be seen from a comparison between Fig. 1(d) and Fig. 3. In the [110] direction [Fig. 1(d)], $-\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$ is larger than $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$, while the opposite is true in the [111] direction (Fig. 3). Better trial functions must be able to account for the directional dependence.

The obvious way to get a total estimate of the error in Eq. (1) would be to integrate the square of the sum of the two terms in Eq. (1). However, it turns out that with such an estimate, the error for the trial function f_1 is smallest. This is explained by the fact that $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$ calculated from f_1 varies very smoothly with $\mathbf{q}$, while it varies more rapidly when it is calculated with the trial functions that contain the group velocity. With the latter trial functions there are a few points with a large discrepancy that contribute a large portion to the sum of squares. To avoid this difficulty we choose to integrate over the absolute value of the two terms,

$$\sigma = \int d\mathbf{q}|\dot{N}_{\mathrm{drift}}(\mathbf{q},j) + \dot{N}_{\mathrm{scatt}}(\mathbf{q},j)|. \tag{18}$$

The result of this error estimate is given in Table II, where the error has been scaled to the value 1 for the trial function f_1. The σ values decreases when better trial functions are used but not very rapidly. λ varies fairly linear with σ, and an extrapolation to $\sigma = 0$ indicates that the λ values would increase with a factor of 3–5 times. Hopefully the error would decrease more rapidly towards zero but it is still quite possible that

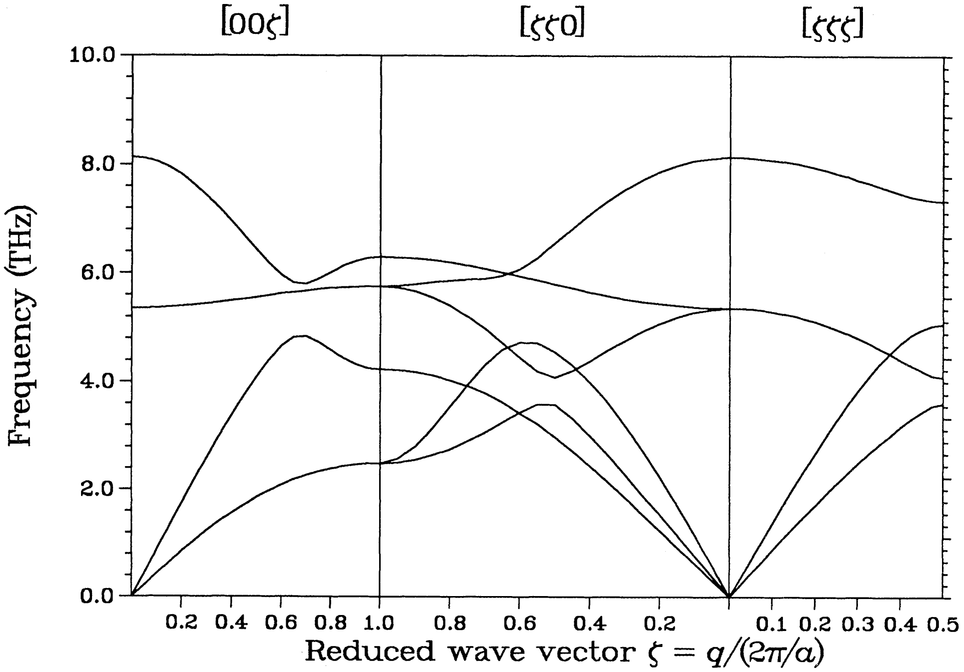

FIG. 2. Phonon dispersion relation for NaCl in certain high-symmetry directions calculated from a deformation-dipole model.

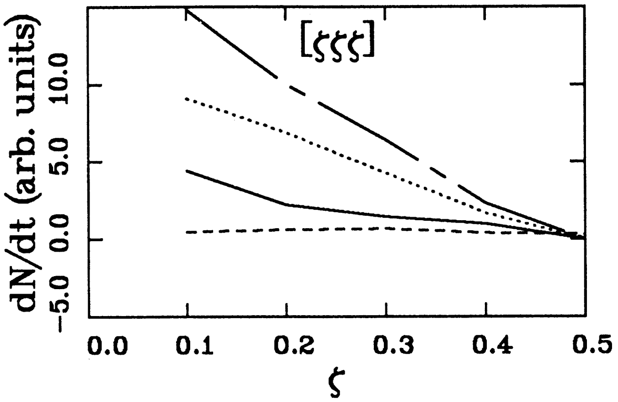

FIG. 3. Comparison of the two terms in Eq. (1) for q vectors in the [111] direction for the TA$_1$ branch in NaCl. $\xi = q/(2\pi/a)$ is the dimensionless reduced-wave-vector coordinate. Solid curve is $-\dot{N}_{\mathrm{drift}}(\mathbf{q},j)$. The other curves are $\dot{N}_{\mathrm{scatt}}(\mathbf{q},j)$ calculated with different trial functions f. The dashed line is obtained from f_1, the dotted line from f_2, and the dot-dashed line is obtained from f_{br}.

the calculated values are by about a factor of 2 below the true value for the model crystals. However, the calculated thermal conductivities are in most cases within ±25% of the experimental values in Table I.

It will probably be very difficult to invent better trial functions and at the same time keep the number of variational constants at a reasonable level. Further progress in finding the correct solution to the Boltzmann equation will probably be made by employing some iteration method to find a numerical solution. The starting point for the iteration could be the best trial function that has been found in the present calculations. Such an approach will require a lot of computer time.

VI. CONCLUSIONS

The thermal-conductivity values that are obtained with the best trial functions are greater than the experimental values in eight of the crystals studied. The largest discrepancy is found for LiBr where the theoretical values are 48% higher than the experimental values. Since the variational principle states that the variational solution always gives a lower limit to the true thermal conductivity of the model crystals this indicates that something could be incomplete in the model.

Part of the difference between theory and experiment could be due to uncertainties in the experimental values. This is partly due to the correction of the measured values to constant volume and in part due to the measured values themselves. The maximum error is estimated to 10% which can acount for the differences in some crystals but not in LiBr, NaF, NaI, KCl, and RbBr. The error estimates that were made in the preceding section indicate that it is very possible that the true thermal conductivity of the model crystal could be a factor-of-2 (or more) higher than the values that were presented in Tables I and II. This implies that there are parts of the theory that have to be modified. Three areas where more work needs to be done will be suggested.

A great uncertainty in the calculations lies in the value of C_{111} which appears squared in the final expression. This third-order derivative of the potential energy of a pair of nearest neighbors is calculated from a potential consisting of a Coulomb part and a Born-Mayer part. The parameters in the Born-Mayer potential are fitted to the lattice constant and the elastic constants. The value for C_{111} is very sensitive to the input values as well as to what assumptions are made about next-nearest-neighbor interactions. This could result in uncertainties in the calculated thermal-conductivity values as high as ±50%.

In LiBr, LiI, NaI, RbF, and CsF, an appreciable amount of next-nearest-neighbor interactions between the larger ions is expected. This has not been included in the calculations of the scattering matrix elements but it has been included in the calculation of the dispersion relations in LiBr and LiI.

It has been observed[29] that there is a significant deviation from the high temperature T^{-1} dependence in KCl, KI, RbBr, and RbI even after correction for thermal-expansion effects. The decrease in the thermal conductivity with temperature is faster than T^{-1} in these crystals, which indicates that there can be important contributions from four-phonon scattering processes. Inclusion of higher-order scattering processes could lower the calculated λ values.

VII. SUMMARY

In crystals with a high mass ratio, the calculated thermal-conductivity values increases dramatically (by 50–150%), when separate trial functions for the acoustic and optic branches are used. In crystals with a mass ratio near 1, the corresponding increase in the thermal conductivity values is approximately 10%. With separate trial functions for the acoustic and optic branches it is found that the optic phonons carry 2–34% of the heat. Optic phonons carry approximately 34% of the heat in NaF and KCl while they carry almost no heat in RbF and CsF.

The frequency dependence for the optic trial function should be chosen so that it corresponds to $\tau \propto \omega^{-k}$, where k=2 or somewhat higher. This does not apply to LiBr and LiI where k should be equal to 1.

The estimates of the error in the solution to the Boltzmann equation indicate that the true thermal conductivity of the model crystals is at least twice as high as the values that have been obtained in this calculation. If that estimate is correct, the theoretical thermal conductivity would be much higher than the experimental values and certain parts of the theory would have to be modified. Three possible causes to the error are the value of the third-order derivative of the potential energy C_{111}, the neglect of next-nearest-neighbor interactions in crystals with a high mass ratio, and the neglect of higher-order scattering processes. More work needs to be done in these areas.

The error estimates also show that it will be very difficult to find better trial functions. A correct solution to the Boltzmann equation is probably best found by some iterative method.

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