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Calculation of the complementary variational modified bounds on the phonon thermal conductivity

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Abstract. The complementary variational principle is used to derive suitable expressions for the first modified bounds on the phonon thermal conductivity. The variational trial function is taken to depend on a series of variational parameters. It is shown that the relations needed to select one decomposition of the collision operator in preference to the others are independent of the number of variational parameters. The convergence of the method is investigated both analytically and numerically when the number of variational parameters is increased. All types of phonon interactions are considered and the results agree quantitatively with the experimental data for Ge and LiF over a wide temperature range.

1. Introduction

The ordinary and complementary variational principles have been used frequently in solving the linearized phonon Boltzmann equation. The ordinary variational principle determines only a lower bound on the phonon thermal conductivity [1–5]. The complementary variational principle has the advantage that it determines a series of modified lower bounds as well as a series of upper bounds [6–12]. Both series converge to the exact value of the phonon thermal conductivity.

Most of the calculations of the ordinary lower bound and all the calculations of the complementary modified bounds have been performed by using a variational trial function that depends on one variational parameter and is proportional to the component of the phonon wavevector k in the direction of the applied temperature gradient. This form of the trial function gives reasonable results only when three-phonon normal processes dominate the phonon scattering mechanism. Hamilton and Parrott [3] used a more general trial function for the calculation of the ordinary lower bound. Their function depends on a series of variational parameters and gives reasonable results over a wide temperature range when all types of phonon interactions are taken into consideration.

The aim of the present work is to calculate the complementary first modified lower and upper bounds by using a trial function of the type used in [3]. The first modified lower bound gives higher values than those obtained from the ordinary lower bound and is thus a better approximation for the phonon thermal conductivity. Also, the results of the complementary variational principle are expected to converge much faster than the results of the ordinary principle when the number of variational parameters increases.

The complementary variational principle requires that the phonon collision operator should be decomposed into two operators that are linear, symmetric and either positive or negative semidefinite and such that at least one of them possesses an inverse. The best way of decomposing the collision operator for both the sequences of lower and upper bounds

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is explored in the present work by using quite a general variational function, which can be expanded in terms of the elements of a general basis with the coefficients of expansion as the variational parameters. The treatment shows that the relations obtained in [12] using a variational function that depends on one variational parameter will remain valid in this general case. The convergence of the method when the number of variational parameters increases is proved analytically by using this general trial function. It has been shown that the first modified lower bound increases monotonically as the number of variational parameters is increased, while the first modified upper bound decreases. This indicates that both bounds approach the exact value. The analysis is also valid for the ordinary lower bound. To the best of our knowledge this seems to be the first rigorous attempt to study analytically the convergence due to the increase of the number of variational parameters.

For the rest of the calculations the same variational trial function as used in [3] has been utilized. The elements of the basis of the expansion are accordingly taken as powers of k multiplied by the cosine of the angle between k and the temperature gradient. Also, the isotropic model of Hamilton and Parrott [3, 13] is utilized to deal with Umklapp processes. The reciprocal lattice vector involved in the Umklapp processes for which the phonon under consideration is created (or destroyed) and two other phonons are destroyed (or created) is taken in the form suggested by Mikhail and Madkour [14], which seems to be more reasonable than the corresponding form used in earlier treatments for the calculation of modified bounds [9, 10]. We have further used the correct areas and limits of the integrals given in [14] for the normal and Umklapp processes of this type of interaction. The general expressions for the tensors that determine the strength of all types of three-phonon interactions are also utilized instead of the simple forms used in previous work. All types of phonon interactions are included and the numerical calculations are performed over a wide temperature range. The convergence of the method has further been confirmed numerically. The present modifications have considerably improved the results of the first modified lower bound, which showed a good quantitative agreement with the experimental data of germanium (Ge) and lithium fluoride (LiF). The modified upper bound was not considered in this part of the paper for reasons discussed in section 4.

The present work is arranged in the following way. In section 2 the general expressions for the sequences of lower and upper bounds are given. The first modified lower and upper bounds are considered in section 3 by using a general variational trial function. The quantities needed for the calculation of the first modified lower bound by using a power-series trial function are dealt with in section 4 when normal and Umklapp processes occur alone. Section 5 is devoted to considering the effect of other types of phonon interactions. The details of the numerical calculations and the results of the experimental applications are discussed in section 6. Finally the expressions for some basic coefficients are given in an appendix.

2. Basic relations

The linearized phonon Boltzmann equation takes the form [15]

$$X = \hat{H}\phi \tag{1a}$$

$$X \equiv \{X_\nu\} \qquad \phi \equiv \{\phi_\nu\} \qquad \nu = (\sigma, k) \tag{1b}$$

where σ and k are the phonon polarization and wavevector. The left-hand side of equation (1a) results from the drift motion of the phonons. In the presence of a temperature

gradient ∇T, X_ν takes the form

$$X_\nu = -\boldsymbol{v}_\nu \cdot \nabla T g_\nu E_\nu / k_B T^2 \qquad E_\nu = \hbar\omega_\nu \tag{2}$$

where k_B is the Boltzmann constant, T is the temperature and v_ν, ω_ν and E_ν are the phonon group velocity, angular frequency and energy. The right-hand side of equation (1*a*) is the collision term, which represents all types of collisions that phonons undergo in dielectric materials. ϕ_ν is a measure of the small deviation of the phonon distribution N_ν from the Bose–Einstein equilibrium distribution $\bar{N}_\nu$ and is defined by

$$N_\nu = \bar{N}_\nu + g_\nu \phi_\nu \qquad g_\nu = \bar{N}_\nu(1 + \bar{N}_\nu). \tag{3}$$

Also, $\hat{H}$ is a linear operator, the specific form of which is given in sections 4 and 5 for the different types of phonon interactions. It is readily shown that $\hat{H}$ is, in general, symmetric and positive semidefinite with respect to the inner product

$$\langle \psi, \theta \rangle = \sum_\nu \psi_\nu \theta_\nu \tag{4a}$$

where ψ and θ are any two elements of the Hilbert space of all functions of ν. Also $\hat{H}$ can be expressed for all types of interactions and any ψ in the form

$$(\hat{H}\psi)_\nu = \sum_{\nu'} H_{\nu\nu'} \psi_{\nu'} \qquad H_{\nu\nu'} = H_{\nu'\nu}. \tag{4b}$$

Moreover, in the present work only the acoustic polarization branches will be considered, dispersion will be neglected, the medium will be assumed to be isotropic and the elastic continuum model will be utilized. Accordingly

$$\begin{aligned} &v_\nu = v_\sigma \boldsymbol{k}^* \qquad \omega_\nu = v_\sigma k \qquad \sigma = t, \ell \\ &v_t = (\mu/\rho)^{1/2} \qquad v_\ell = [(\lambda + 2\mu)/\rho]^{1/2} \end{aligned} \tag{5}$$

where $\boldsymbol{k}^*$ is a unit vector in the direction of $\boldsymbol{k}$, t and ℓ refer to transverse and longitudinal branches, ρ is the equilibrium mass density, and λ and μ are the Lamé constants.

Different methods are adopted to solve equation (1). The variational method has the advantage that one does not need the exact solution. A variational trial function ψ that depends on some variational parameters will be assumed as a solution. The values of these parameters will then be chosen so that a certain functional takes its maximum or minimum value. The most familiar form of the functional is given by [1]

$$F(\psi) = 2\langle \psi, \boldsymbol{X} \rangle - \langle \psi, \hat{H}\psi \rangle. \tag{6}$$

The exact solution ϕ of the Boltzmann equation maximizes F with a value $F(\phi) = \langle \phi, \boldsymbol{X} \rangle$. If we further assume that ψ depends on one variational parameter ($\psi \equiv a\psi$) and take $\partial F/\partial a = 0$, then

$$F(\psi) = \langle \psi, \boldsymbol{X} \rangle^2 / \langle \psi, \hat{H}\psi \rangle. \tag{7}$$

This is identical with the expression originally used by Ziman [2]. Ziman used a trial function of the form

$$\psi_\nu = \boldsymbol{u} \cdot \boldsymbol{k} \qquad \boldsymbol{u} = -\nabla T / T. \tag{8}$$

Also, the phonon thermal conductivity is given by [15]

$$\kappa = \frac{k_B T^2}{N_0 \Omega |\nabla T|^2} \chi \qquad \chi = \langle \phi, X \rangle = \frac{\langle \phi, X \rangle^2}{\langle \phi, \hat{H} \phi \rangle} \tag{9}$$

where N_0 is the number of unit cells in the crystal and Ω is the volume of a unit cell. It is therefore clear that the two identical maximum values of the two functionals defined by (6) and (7) that result at $\psi = \phi$ are directly proportional to the thermal conductivity. Thus for any trial function ψ, the functional $F(\psi)$ determines a lower bound $\kappa^<(\psi)$ on the thermal conductivity, where

$$\kappa^<(\psi) = \frac{k_B T^2}{N_0 \Omega |\nabla T|^2} \chi^<(\psi) \qquad \chi^<(\psi) = F(\psi). \tag{10}$$

The lower bound obtained by using the variational trial function defined by (8) and the functional (7) is usually called the Ziman limit.

The results of the ordinary variational principle discussed above have been improved along the following two directions:

(i) More general variational trial functions than the one given in (8) were used. Hamilton and Parrott [3] chose ψ_v in the form of a power series in k as

$$\psi_v = k^* \cdot u \sum_{r=1}^{r_{\max}} a_r^\sigma x^r \qquad x = k/k_D. \tag{11}$$

Here a_r^σ are the variational parameters, $r_{\max}$ is the highest power in the series and k_D is the radius of the Debye sphere.

(ii) The complementary variational principle was utilized. This method yields a sequence of lower bounds as well as a sequence of upper bounds on the phonon thermal conductivity. According to Jensen *et al* [6], Benin [7], Srivastava [8] and Mikhail [12] the sequence of lower bounds is given by

$$\kappa_m^<(\hat{J}, \psi) = \frac{k_B T^2}{N_0 \Omega |\nabla T|^2} \chi_m^<(\hat{J}, \psi) \qquad m = 0, 1, 2, \ldots \tag{12a}$$

where

$$\chi_m^<(\hat{J}, \psi) = 2\langle \psi, \hat{A}^m X \rangle - \langle \psi, \hat{A}^m \hat{H} \psi \rangle + \langle X, \hat{H}^{-1}(\hat{I} - \hat{A}^m) X \rangle \tag{12b}$$

$$\hat{H} = \hat{J} - \hat{L} \qquad \hat{A} = \hat{I} - \hat{H}\hat{J}^{-1} = \hat{L}\hat{J}^{-1}. \tag{12c}$$

Also, the sequence of upper bounds is given by

$$\kappa_m^>(\hat{J}, \psi) = \frac{k_B T^2}{N_0 \Omega |\nabla T|^2} \chi_m^>(\hat{J}, \psi) \qquad m = 1, 3, 5, \ldots \tag{13a}$$

where

$$\chi_m^>(\hat{J}, \psi) = \langle \psi, \hat{A}^m \hat{H} \psi \rangle - 2\langle \psi, \hat{A}^m X \rangle + \langle X, \hat{H}^{-1}(\hat{I} + \hat{A}^m) X \rangle \tag{13b}$$

$$\hat{H} = \hat{J} + \hat{L} \qquad \hat{A} = \hat{H}\hat{J}^{-1} - \hat{I} = \hat{L}\hat{J}^{-1}. \tag{13c}$$

In the two sets of equations $\hat{I}$ is the identity operator, $\hat{J}$ and $\hat{L}$ are linear operators, positive semidefinite and symmetric with respect to the inner product defined by (4*a*), and $\hat{J}$ possesses an inverse. Also, according to [12] the sequence of lower bounds will always converge to the exact limit when $m \to \infty$, while the sequence of upper bounds converges subject to the condition that the eigenvalues of the operator $\hat{J}^{-1}\hat{L}$ exist within the interval (0, 1) or alternatively the eigenvalues of $\hat{J}^{-1}\hat{H}$ exist within (1, 2). The operators $\hat{J}$ and $\hat{L}$ can be chosen arbitrarily subject to these restrictions, so that (12*c*) is satisfied for the sequence of lower bounds and (13*c*) is satisfied for the sequence of the upper bounds. Moreover, if ψ depends on one variational parameter, then

$$\chi_m^<(\hat{J}, \psi) = \langle X, \hat{H}^{-1}(\hat{I} - \hat{A}^m)X\rangle + \langle \psi, \hat{A}^m X\rangle^2/\langle \psi, \hat{A}^m \hat{H}\psi\rangle \tag{14a}$$

$$\chi_m^>(\hat{J}, \psi) = \langle X, \hat{H}^{-1}(\hat{I} + \hat{A}^m)X\rangle - \langle \psi, \hat{A}^m X\rangle^2/\langle \psi, \hat{A}^m \hat{H}\psi\rangle. \tag{14b}$$

In all previous work the above two approaches were not employed together. The ordinary variational method was used with a trial function of the form (11) [3], while the first modified bounds were dealt with by using the simpler form (8) [9, 10, 12], which is only valid when normal processes dominate the phonon scattering mechanism. The main motivation of the present work is to consider the first modified bounds retrieved from the complementary variational principle by using the more general trial function (11).

3. First modified bounds

The first modified lower and upper bounds are given by equations (12*a*) and (13*a*) with $m = 1$. $\chi_1^<$ and $\chi_1^>$ are defined by (14*a*, *b*) when the trial function depends on one variational parameter (equation (8)), while they are defined by (12*b*) and (13*b*) when the trial function depends on more than one variational parameter (equation (11)). The latter case is the case considered here, and thus

$$\chi_1^<(\hat{J}, \psi) = 2\langle \psi, (\hat{I} - \hat{H}\hat{J}^{-1})X\rangle - \langle \psi, (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi\rangle + \langle X, \hat{J}^{-1}X\rangle \tag{15a}$$

$$\chi_1^>(\hat{J}, \psi) = -2\langle \psi, (\hat{H}\hat{J}^{-1} - \hat{I})X\rangle + \langle \psi, (\hat{H}\hat{J}^{-1} - \hat{I})\hat{H}\psi\rangle + \langle X, \hat{J}^{-1}X\rangle. \tag{15b}$$

The decomposition of $\hat{H}$ in (15*b*) differs from that in (15*a*) and accordingly the two equations are not identical. In this section we consider some general relations that do not depend on the explicit form of $\hat{H}$ and $\hat{J}$. They will also be proved for a more general trial function than the one given in (11). The trial function will be taken in the form

$$\psi_\nu = \sum_{r=1}^{r_{\max}} a_r^\sigma \theta_{rk} \qquad \text{or equivalently} \qquad \psi_\sigma = \sum_{r=1}^{r_{\max}} a_r^\sigma \theta_r \tag{16}$$

where $\{\theta_r \equiv \{\theta_{rk}\}\}$ is the basis of expansion and $\psi_\sigma \equiv \{\psi_{\sigma k} \equiv \psi_\nu$, for a fixed $\sigma\}$. The quantities that depend on ψ in (15*a*, *b*) can then be expressed as

$$\langle \psi, X\rangle = \sum_{r\sigma} a_r^\sigma [\theta_r, X_\sigma] \qquad \langle \psi, \hat{H}\hat{J}^{-1}X\rangle = \sum_{r\sigma} a_r^\sigma [\theta_r, (\hat{H}\hat{J}^{-1}X)_\sigma]$$

$$\langle \psi, \hat{H}\psi\rangle = \sum_{r\sigma}\sum_{r'\sigma'} a_r^\sigma a_{r'}^{\sigma'} [\theta_r, \hat{H}_{\sigma\sigma'}\theta_{r'}] \tag{17}$$

$$\langle \psi, \hat{H}\hat{J}^{-1}\hat{H}\psi\rangle = \sum_{r\sigma}\sum_{r'\sigma'} a_r^\sigma a_{r'}^{\sigma'} \langle h_r^\sigma, \hat{J}^{-1}h_{r'}^{\sigma'}\rangle$$

where

$$(h_{r'}^{\sigma'})_\nu = (\hat{H}_{\sigma\sigma'}\theta_{r'})_k \tag{18a}$$

$$[\alpha, \beta] = \sum_k \alpha_k \beta_k \qquad (\hat{H}_{\sigma\sigma'}\alpha)_k = \sum_{k'} H_{\sigma\sigma' kk'}\alpha_{k'} \tag{18b}$$

α and β are two elements of the Hilbert space of all functions of k, and $H_{\sigma\sigma' kk'} = H_{\nu\nu'}$. All the vector quantities with subscript σ are defined in the same way as ψ_σ. Also, the operator $\hat{H}_{\sigma\sigma'}$ is related to the original collision operator $\hat{H}$ by

$$(\hat{H}\psi)_\nu = \sum_{\sigma'} (\hat{H}_{\sigma\sigma'}\psi_{\sigma'})_k \qquad (\hat{H}\psi)_\sigma = \sum_{\sigma'} \hat{H}_{\sigma\sigma'}\psi_{\sigma'}. \tag{19}$$

It can further be shown that

$$[\alpha, \hat{H}_{\sigma\sigma'}\beta] = [\hat{H}_{\sigma'\sigma}\alpha, \beta]. \tag{20}$$

The calculations in the rest of this section will be confined to the first modified lower bound. The final analogous results of the first upper bound will be given subsequently.

The best set of parameters a_r^σ $(r = 1, 2, \ldots, r_{\max})$ is the one that maximizes $\kappa_1^<(\hat{J}, \psi)$. They are thus inferred by taking $\partial\chi_1^</\partial a_r^\sigma = 0$ and accordingly determined from

$$Z_r^\sigma = \sum_{\sigma' r'} G_{rr'}^{\sigma\sigma'} a_{r'}^{\sigma'} \tag{21}$$

where

$$\begin{aligned} Z_r^\sigma &= [\theta_r, ((\hat{I} - \hat{H}\hat{J}^{-1})X)_\sigma] \\ G_{rr'}^{\sigma\sigma'} &= [\theta_r, \hat{H}_{\sigma\sigma'}\theta_{r'}] - \langle h_r^\sigma, \hat{J}^{-1}h_{r'}^{\sigma'}\rangle. \end{aligned} \tag{22}$$

Equations (16), (18*a*), (19), (20), (21) and (22) in addition to the relation

$$\sum_{\sigma'} \hat{H}_{\sigma\sigma'}(\hat{J}^{-1}\hat{H}\psi)_{\sigma'} = (\hat{H}\hat{J}^{-1}\hat{H}\psi)_\sigma$$

yield

$$[\theta_r, ((\hat{I} - \hat{H}\hat{J}^{-1})X)_\sigma] = [\theta_r, ((\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi)_\sigma] \tag{23a}$$

and

$$\langle\psi, (\hat{I} - \hat{H}\hat{J}^{-1})X\rangle = \langle\psi, (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi\rangle. \tag{23b}$$

Substitution of (23*b*) in (15*a*) gives

$$\begin{aligned} \chi_1^<(\hat{J}, \psi) &= \langle\psi, (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi\rangle + \langle X, \hat{J}^{-1}X\rangle \\ &= \langle\psi, (\hat{I} - \hat{H}\hat{J}^{-1})X\rangle + \langle X, \hat{J}^{-1}X\rangle. \end{aligned} \tag{24}$$

The first modified lower bound on the thermal conductivity is now given by (12*a*) and (24) with the values of the adjustable parameters a_r^σ being determined from (21). As regards the first modified upper bound, it can be shown that the set of adjustable parameters $\{a_r^\sigma\}$ that minimizes $\kappa_1^>(\hat{J}, \psi)$ and the minimum value of $\kappa_1^>(J, \psi)$ are determined from equations similar to (21), (22) and (24). The results would preferably be expressed in terms of $(\hat{H}\hat{J}^{-1} - \hat{I})$ instead of $(\hat{I} - \hat{H}\hat{J}^{-1})$. We now proceed to consider the following three points:

(i) In order to emphasize further that the first modified lower bound determined in this way takes its maximum value, we consider another trial function ψ' that can be expanded in terms of the basis $\{\theta_r\}$ as

$$\psi'_\nu = \sum_{r=1}^{r_{\max}} a_r'^{\sigma} \theta_{rk}. \tag{25}$$

It can then be shown by multiplying (23*a*) by $a_r'^{\sigma}$ and summing over r, σ that

$$\langle \psi', (\hat{I} - \hat{H}\hat{J}^{-1})\boldsymbol{X}\rangle = \langle \psi', (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi\rangle. \tag{26}$$

Consequently

$$\chi_1^<(\hat{J}, \psi) - \chi_1^<(\hat{J}, \psi') = \langle \psi, \hat{H}_1\psi\rangle - 2\langle \psi', \hat{H}_1\psi\rangle + \langle \psi', \hat{H}_1\psi'\rangle \tag{27}$$

where $\hat{H}_1 = (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}$ and $\chi_1^<(\hat{J}, \psi')$ is defined from (15*a*) after replacing ψ by ψ' while $\chi_1^<(\hat{J}, \psi)$ is defined directly from (24). Also, it was readily shown [6, 12] that the operator $\hat{H}_1$ is positive semidefinite and symmetric. This, in turn, leads to the Cauchy–Schwarz inequality

$$\langle \psi', \hat{H}_1\psi\rangle \leqslant |\langle \psi', \hat{H}_1\psi\rangle| \leqslant (\langle \psi, \hat{H}_1\psi\rangle\langle \psi', H_1\psi'\rangle)^{1/2} \tag{28}$$

which implies that the right-hand side of (27) is positive and accordingly

$$\chi_1^<(\hat{J}, \psi) \geqslant \chi_1^<(\hat{J}, \psi') \tag{29}$$

for any ψ'. This confirms that the trial function ψ defined by (16) and (21) indeed maximizes $\kappa_1^<(\hat{J}, \psi)$.

(ii) Another important point that is worth investigating is how to select $\hat{J}$. The form of $\hat{J}$ depends on the way in which $\hat{H}$ is decomposed into the form (12*c*). As has been pointed out previously, the operator $\hat{H}$ can be decomposed in this form in many ways, and it is clearly desirable to present a method of selecting the best of these ways. Srivastava [8] used a semi-rigorous argument to choose one decomposition in preference to others. Mikhail [12] presented a more accurate method. The two treatments, however, were carried out for the simple case in which ψ depends on one variational parameter. In the following it will be shown that Mikhail's procedure can be generalized and his result will remain valid in the present case in which ψ depends on a series of variational parameters. For this purpose we consider the following two decompositions:

$$\hat{H} = \hat{J} - \hat{L} \qquad \text{and} \qquad \hat{H} = \hat{\Gamma} - \hat{\Lambda} \tag{30}$$

so that the operators $\hat{\Gamma}$ and $\hat{\Lambda}$ possess the same properties as $\hat{J}$ and $\hat{L}$ respectively. For the second decomposition and for a variational trial function

$$\xi_\nu = \sum_r b_r^{\sigma} \theta_{rk}$$

the first modified lower bound is given by

$$\kappa_1^<(\hat{\Gamma}, \xi) = \frac{k_B T^2}{N_0 \Omega |\nabla T|^2} \chi_1^<(\hat{\Gamma}, \xi). \tag{31}$$

Here $\chi_1^<(\hat{\Gamma}, \xi)$ takes the same form as (15*a*) but with $\hat{J}$ and ψ being replaced respectively by $\hat{\Gamma}$ and ξ. Also, the adjustable parameters b_r^σ have to be chosen so that ξ maximizes $\kappa_1^<(\hat{\Gamma}, \xi)$. Hence, the analogous equations to (23*b*) and (24) take the form

$$\langle \xi, (\hat{I} - \hat{H}\hat{\Gamma}^{-1})X\rangle = \langle \xi, (\hat{I} - \hat{H}\hat{\Gamma}^{-1})\hat{H}\xi\rangle \tag{32a}$$

and

$$\chi_1^<(\hat{\Gamma}, \xi) = \langle \xi, (\hat{I} - \hat{H}\hat{\Gamma}^{-1})\hat{H}\xi\rangle + (X, \hat{\Gamma}^{-1}X). \tag{32b}$$

It also follows from (29) that

$$\chi_1^<(\hat{J}, \psi) \geqslant \chi_1^<(\hat{J}, \xi) \tag{33a}$$

which, in turn, implies that

$$\chi_1^<(\hat{J}, \psi) \geqslant 2\langle \xi, (\hat{I} - \hat{H}\hat{J}^{-1})X\rangle - \langle \xi, (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\xi\rangle + (X, \hat{J}^{-1}X). \tag{33b}$$

We now introduce the operator $\hat{S} = \hat{J}^{-1} - \hat{\Gamma}^{-1}$ and make use of (32*a*, *b*) to express (33*b*) in the form

$$\chi_1^<(\hat{J}, \psi) \geqslant \chi_1^<(\hat{\Gamma}, \xi) + \{\langle \hat{H}\xi, \hat{S}\hat{H}\xi\rangle - 2\langle \hat{H}\xi, \hat{S}X\rangle + (X, \hat{S}X)\}. \tag{34}$$

The operator $\hat{S}$ is symmetric and we shall further assume that it is positive semidefinite. Accordingly, the following Cauchy–Schwarz inequality holds:

$$\langle \hat{H}\xi, \hat{S}X\rangle \leqslant |\langle \hat{H}\xi, \hat{S}X\rangle| \leqslant (\langle \hat{H}\xi, \hat{S}\hat{H}\xi\rangle\langle X, \hat{S}X\rangle)^{1/2}. \tag{35}$$

Hence the quantity between the curly brackets $\{\ldots\}$ on the right-hand side of (34) is positive and thus

$$\chi_1^<(\hat{J}, \psi) \geqslant \chi_1^<(\hat{\Gamma}, \xi). \tag{36}$$

The above result is obtained subject to the condition that $\hat{S}$ is positive semidefinite. It can, therefore, be concluded that the first decomposition of $\hat{H}$ in (30) gives rise to a better lower bound on κ than the second decomposition if $\hat{J}^{-1} - \hat{\Gamma}^{-1}$ is positive semidefinite. This generalizes the result of Mikhail [12], which was obtained for the special case of a trial function that depends on one variational parameter.

It can be shown in a similar manner that the decomposition $\hat{H} = \hat{J} + \hat{L}$ gives a better first modified upper bound than the decomposition $\hat{H} = \hat{\Gamma} + \hat{\Lambda}$ if the operator $\hat{\Gamma}^{-1} - \hat{J}^{-1}$ is positive semidefinite.

(iii) The calculation of the first modified lower bound from equation (24) necessitates that one has to solve equation (21) numerically for a certain number of variational parameters a_r^σ ($r = 1, 2, \ldots, r_{\max}$; $\sigma = t, \ell$) to find their values. In other words it is required to evaluate numerically the reciprocal of the matrix $\{G_{rr'}^{\sigma\sigma'}\}$ ($r, r' = 1, 2, \ldots, r_{\max}$; $\sigma, \sigma' = t, \ell$) for a given $r_{\max}$. However, in the simplest case of $r_{\max} = 1$ we only have two variational parameters (a_1^t, a_1^ℓ) and the solution of equation (21) may be obtained analytically. The corresponding expression for $\chi_1^<$ can be retrieved from equation (24). It takes the form

$$\chi_1^<(\hat{J}, \psi, r_{\max} = 1) = d^{-1}[G_{11}^{\ell\ell}(Z_1^t)^2 - 2G_{11}^{t\ell}Z_1^tZ_1^\ell + G_{11}^{tt}(Z_1^\ell)^2] + (X, \hat{J}^{-1}X) \tag{37a}$$

where

$$d = G_{11}^{tt} G_{11}^{\ell\ell} - (G_{11}^{t\ell})^2. \tag{37b}$$

In the case of one variational parameter $\chi_1^<$ is given by (14*a*) with $m = 1$ and $\psi \equiv \theta_1$. Consequently

$$\chi_1^<(\hat{J}, \psi \equiv \theta_1) = \left(\sum_\sigma Z_1^\sigma \right)^2 \Big/ \sum_{\sigma\sigma'} G_{11}^{\sigma\sigma'} + \langle \boldsymbol{X}, \hat{J}^{-1} \boldsymbol{X} \rangle. \tag{38}$$

It can then be shown that

$$\chi_1^<(\hat{J}, \psi, r_{\max} = 1) - \chi_1^<(\hat{J}, \psi \equiv \theta_1)$$
$$= \left(d \sum_{\sigma\sigma'} G_{11}^{\sigma\sigma'} \right)^{-1} [Z_1^t (2G_{11}^{t\ell} + G_{11}^{\ell\ell}) - Z_1^\ell (2G_{11}^{tt} + G_{11}^{t\ell})]^2. \tag{39}$$

The matrix $\{G_{rr'}^{\sigma\sigma'}\}$ $(r, r' = 1, 2, \ldots, r_{\max};\ \sigma, \sigma' = t, \ell)$ is positive definite for any value of $r_{\max}$, a fact that follows directly from the positive semidefinite property of the operator $\hat{H}_1 = (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}$ and from the relation

$$\langle \psi, (\hat{I} - \hat{H}\hat{J}^{-1})\hat{H}\psi \rangle = \sum_{\substack{\sigma\sigma' \\ rr'}} a_r^\sigma a_{r'}^{\sigma'} G_{rr'}^{\sigma\sigma'} \tag{40}$$

which is valid for any ψ that can be expanded in the form (16). It thus follows that the right-hand side of (39) is positive and accordingly

$$\chi_1^<(\hat{J}, \psi, r_{\max} = 1) > \chi_1^<(\hat{J}, \psi \equiv \theta_1). \tag{41}$$

This indicates that $\kappa_1^<(\hat{J}, \psi, r_{\max} = 1)$ yields better values for the thermal conductivity than $\kappa_1^<(\hat{J}, \psi \equiv \theta_1)$, which is expected since the former depends on two variational parameters while the latter depends on one variational parameter only. One should further expect that the increase of $r_{\max}$ leads to a continual improvement in the calculated values of the thermal conductivity and that $\kappa_1^<(\hat{J}, \psi)$ approaches the exact solution when $r_{\max} \to \infty$. In order to confirm this we first note from (21), (24) and (40) that

$$\chi_1^<(\hat{J}, \psi) = Z^{\mathrm{T}} \mathbf{G}^{-1} Z + \langle \boldsymbol{X}, \hat{J}^{-1} \boldsymbol{X} \rangle \tag{42}$$

where $\mathbf{G}$ and Z refer respectively to the matrix $\{G_{rr'}^{\sigma\sigma'}\}$ $(r, r' = 1, 2, \ldots, r_{\max};\ \sigma, \sigma' = t, \ell)$ and the column vector $\{Z_r^\sigma\}$ $(r = 1, 2, \ldots, r_{\max};\ \sigma = t, \ell)$, while the superscript T refers to the transpose. We then utilize the following formula, which depends on the partition of matrices [16, 17]:

$$(Z^{\mathrm{T}} \mathbf{G}^{-1} Z)_{r_{\max} = s+1} = (Z^{\mathrm{T}} \mathbf{G}^{-1} Z)_{r_{\max} = s} + W_s^{\mathrm{T}} \Omega_s W_s \tag{43}$$

where

$$W_s = Z_s - \Lambda_s (\mathbf{G}^{-1} Z)_{r_{\max} = s}$$
$$\Omega_s = \begin{bmatrix} (G^{-1})_{s+1,s+1}^{tt} & (G^{-1})_{s+1,s+1}^{t\ell} \\ (G^{-1})_{s+1,s+1}^{\ell t} & (G^{-1})_{s+1,s+1}^{\ell\ell} \end{bmatrix} \qquad Z_s = \begin{bmatrix} Z_{s+1}^t \\ Z_{s+1}^\ell \end{bmatrix} \tag{44}$$
$$\Lambda_s = \begin{bmatrix} G_{s+1,1}^{tt} & G_{s+1,1}^{t\ell} & \cdots & G_{s+1,s}^{tt} & G_{s+1,s}^{t\ell} \\ G_{s+1,1}^{\ell t} & G_{s+1,1}^{\ell\ell} & \cdots & G_{s+1,s}^{\ell t} & G_{s+1,s}^{\ell\ell} \end{bmatrix}.$$

The fact that $\mathbf{G}$ is positive definite implies that $\mathbf{G}^{-1}$ and consequently Ω_s are also positive definite. As a result the second term on the right-hand side of (43) is always positive and hence

$$(Z^{\mathrm{T}}\mathbf{G}^{-1}Z)_{r_{\max}=s+1} > (Z^{\mathrm{T}}\mathbf{G}^{-1}Z)_{r_{\max}=s}. \tag{45}$$

The last relation together with (42) and (12*a*) imply that the sequence $\{\kappa_1^<(\hat{J},\psi), r_{\max} = 1,2,3,\ldots\}$ increases monotonically as $r_{\max}$ increases. It, therefore, approaches the exact analytical thermal conductivity from below and converges when $r_{\max} \to \infty$. The limit may, however, differ from the exact value.

A similar procedure shows that the sequence $\{\kappa_1^>(\hat{J},\psi), r_{\max} = 1,2,3,\ldots\}$ is monotonically decreasing and accordingly it converges. The limit is above or equal to the exact value.

4. Three-phonon interactions

The analysis presented in the previous two sections depends mainly on the form of the phonon collision operator $\hat{H}$ and on the way in which $\hat{H}$ is decomposed into the forms (12*c*) and (13*c*). In this section we consider that the phonon scattering mechanism is only due to three-phonon normal and Umklapp interactions. The other types of phonon interactions will be dealt with in the following section. The collision operator of three-phonon interactions can be expressed as

$$(\hat{H}_{3\mathrm{p}}\phi)_\nu = \sum_g \left(\sum_{\nu'\nu''} (\phi_\nu + \phi_{\nu'} - \phi_{\nu''}) \bar{P}^{\nu''}_{\nu\nu'} + \tfrac{1}{2} \sum_{\nu'\nu''} (\phi_\nu - \phi_{\nu'} - \phi_{\nu''}) \bar{P}^{\nu}_{\nu'\nu''} \right) = \sum_{\nu'} (H_{3\mathrm{p}})_{\nu\nu'} \phi_{\nu'} \tag{46}$$

where

$$(H_{3\mathrm{p}})_{\nu\nu'} = (H_{3\mathrm{p}})_{\sigma\sigma' kk'} = \sum_g \left(\delta_{\nu\nu'} \sum_{\nu''\nu'''} (\bar{P}^{\nu''}_{\nu\nu'''} + \tfrac{1}{2} \bar{P}^{\nu}_{\nu''\nu'''}) - \sum_{\nu''} (\bar{P}^{\nu'}_{\nu\nu''} + \bar{P}^{\nu}_{\nu'\nu''} - \bar{P}^{\nu''}_{\nu\nu'}) \right). \tag{47}$$

The sum $\sum_g$ is taken over all the relevant reciprocal lattice vectors g including $g = \mathbf{0}$ (normal processes)

$$\bar{P}^{\nu''}_{\nu\nu'} = (P^{\nu''}_{\nu\nu'})_{N_\nu = \bar{N}_\nu} \qquad P^{\nu''}_{\nu\nu'} = W^{\nu''}_{\nu\nu'} N_\nu N_{\nu'} (1 + N_{\nu''}) \tag{48}$$

and $P^{\nu''}_{\nu\nu'}$ and $W^{\nu''}_{\nu\nu'}$ are the net and transition probabilities per unit time of the process $\nu + \nu' \to \nu''$. If the elastic continuum model is considered, then $W^{\nu''}_{\nu\nu'}$ is given by [15]

$$W^{\nu''}_{\nu\nu'} = \frac{\pi\hbar}{4\rho^3 N_0 \Omega} \frac{k^2 k'^2 k''^2}{\omega_\nu \omega_{\nu'} \omega_{\nu''}} |A_{\nu\nu'\nu''}|^2 \delta(\omega_{\nu''} - \omega_{\nu'} - \omega_\nu) \delta_{k+k'=k''+g}. \tag{49}$$

Here $A_{\nu\nu'\nu''}$ is a tensor that measures the strength of three-phonon interactions and is symmetric in ν, ν' and ν''. Also, following Parrott [13] and Hamilton and Parrott [3], the Debye isotropic approximation will be used. Thus for the processes $\nu + \nu' \leftrightarrow \nu''$ and $\nu \leftrightarrow \nu' + \nu''$ involved in the first and second parts of (46) we have respectively

$$\begin{aligned} &x, x', x'' \leqslant 1 \qquad \tfrac{1}{2}(1-\epsilon) < |x + x'| < \tfrac{1}{2}(3-\epsilon) \\ &x'' = [1 - (1-\epsilon)/|x+x'|](x+x') \qquad x'' = 1 - \epsilon + \epsilon|x+x'| \\ &g = [(1-\epsilon)k_{\mathrm{D}}/|x+x'|](x+x') = -(1-\epsilon)k_{\mathrm{D}}k''^* \end{aligned} \tag{50a}$$

and

$$x, x', x'' \leqslant 1 \qquad \tfrac{1}{2}(1-\epsilon) < |\boldsymbol{x} - \boldsymbol{x}'| < \tfrac{1}{2}(3-\epsilon)$$
$$\boldsymbol{x}'' = \boldsymbol{x} - \boldsymbol{x}' - (1-\epsilon)\boldsymbol{k}^* \qquad g = -(1-\epsilon)k_D k^* \tag{50b}$$

where ν is a specific mode, $\epsilon = +1$ and -1 for normal and Umklapp processes, respectively, and the form of g used in (50*b*) was originally introduced by Mikhail and Madkour [14].

As regards the decomposition of $\hat{H}$ we follow Benin [7], Srivastava [9] and Mikhail [12] and take for the sequence of lower bounds

$$\hat{J} = \beta \hat{I} \qquad \text{where} \qquad \beta = 3(\Gamma_\nu)_{\max} \tag{51a}$$

and

$$\Gamma_\nu = \sum_g \sum_{\nu'\nu''} (\bar{P}^{\nu''}_{\nu\nu'} + \tfrac{1}{2}\bar{P}^{\nu}_{\nu'\nu''}). \tag{51b}$$

The above result was obtained by taking β to be greater than or equal to the maximum eigenvalue of $\hat{H}$ and applying the Perron–Frobenius theorem [18]. The analogous analysis for the sequence of upper bounds necessitates that one has to find a positive scalar quantity β' that is less than the minimum eigenvalue of $\hat{H}$. Srivastava [9, 19, 20] presented an argument for the existence of β'. On the other hand, Jäckle [21] showed that the spectrum of $\hat{H}$ extends continuously to zero and accordingly no gap exists within which β' may be chosen. In view of this, we preferred to confine ourselves in the present paper to the case of the first modified lower bound and to leave out of consideration the calculation of the first upper bound.

The variational trial function ψ will be taken in the power-series form (11). This is equivalent to taking $\theta_{rk} = -u(\cos\chi)x^r$ in (16), where χ is the angle between ∇T and $\boldsymbol{k}$. The quantities considered in equation (17) would then take the form

$$\langle \psi, \boldsymbol{X} \rangle = u^2 \sum_{\sigma r} a_r^\sigma X_r^\sigma \qquad \langle \psi, \hat{H}\hat{J}^{-1}\boldsymbol{X} \rangle = u^2\beta^{-1} \sum_{\sigma r} a_r^\sigma Y_r^\sigma$$
$$\langle \psi, \hat{H}\psi \rangle = u^2 \sum_{\substack{\sigma\sigma' \\ rr'}} a_r^\sigma a_{r'}^{\sigma'} H_{rr'}^{\sigma\sigma'} \tag{52}$$
$$\langle \psi, \hat{H}\hat{J}^{-1}\hat{H}\psi \rangle = u^2\beta^{-1} \sum_\nu \left(\sum_{\sigma' r'} a_{r'}^{\sigma'} Q_{r'\nu}^{\sigma'} \right)^2 = u^2\beta^{-1} \sum_{\substack{\sigma\sigma' \\ rr'}} a_r^\sigma a_{r'}^{\sigma'} S_{rr'}^{\sigma\sigma'}$$

where

$$X_r^\sigma = \frac{\hbar k_D}{k_B T} v_\sigma^2 \sum_x (\cos^2\chi) x^{r+1} g_\nu$$
$$Y_r^\sigma = \frac{\hbar k_D}{k_B T} \sum_x (\cos\chi) x^r \hat{H}_{3p}(Y_\nu \cos\chi) \qquad Y_\nu = v_\sigma^2 x g_\nu$$
$$H_{rr'}^{\sigma\sigma'} = \sum_{xx'} (\cos\chi\cos\chi') x^r x'^{r'} (H_{3p})_{\nu\nu'} \tag{53}$$
$$Q_{r'\nu}^{\sigma'} = \sum_{x'} (H_{3p})_{\nu\nu'} (\cos\chi') x'^{r'} \qquad S_{rr'}^{\sigma\sigma'} = \sum_{\sigma'' x} Q_{rx\sigma''}^{\sigma} Q_{r'x\sigma''}^{\sigma'}.$$

The quantities needed for the calculation of the first modified lower bound are thus X_r^σ, Y_r^σ, $H_{rr'}^{\sigma\sigma'}$, $Q_{r'\nu}^{\sigma'}$ and $S_{rr'}^{\sigma\sigma'}$ in addition to the quantity Γ_ν, which determines β, and the quantity

$$X = \langle \boldsymbol{X}, \boldsymbol{X} \rangle / u^2 = \left(\frac{\hbar k_D}{k_B T} \right)^2 \sum_{x\sigma} Y_\nu^2 \cos^2 \chi \tag{54a}$$

which is related to the last term in (15*a*) by

$$\langle \boldsymbol{X}, \hat{J}^{-1} \boldsymbol{X} \rangle = u^2 \beta^{-1} X. \tag{54b}$$

Some of these quantities have been considered in earlier work: X_r^σ and $H_{rr'}^{\sigma\sigma'}$ in [3] and Γ_ν in [9, 12, 14]. The other quantities can be dealt with by using similar approaches. The final results are given by

$$X = N_0 \left(\frac{\hbar k_D}{k_B T} \right)^2 \sum_\sigma v_\sigma^4 \int_0^1 x^4 g_\nu^2 \, dx \qquad X_r^\sigma = N_0 \frac{\hbar k_D}{k_B T} v_\sigma^2 \int_0^1 x^{r+3} g_\nu \, dx$$

$$H_{rr'}^{\sigma\sigma'} = \sum_{\sigma''\sigma'''} \left\{ \tfrac{1}{2} \delta_{\sigma\sigma'} \begin{bmatrix} r+r' & 0 & 0 \\ J_1 & 2 & 0 & 0 \\ & \sigma & \sigma'' & \sigma''' \end{bmatrix} + \begin{bmatrix} 0 & 0 & r+r' \\ J_1 & 0 & 0 & 2 \\ & \sigma'' & \sigma''' & \sigma \end{bmatrix} + \begin{bmatrix} 0 & r+r' & 0 \\ J_1 & 0 & 2 & 0 \\ & \sigma''' & \sigma & \sigma'' \end{bmatrix} \right.$$
$$\left. - \delta_{\sigma'\sigma'''} \left[\begin{matrix} r & 0 & r' \\ J_1 & 1 & 0 & 1 \\ & \sigma & \sigma'' & \sigma''' \end{matrix} + \begin{matrix} 0 & r' & r \\ J_1 & 0 & 1 & 1 \\ & \sigma'' & \sigma''' & \sigma \end{matrix} - \begin{matrix} r' & r & 0 \\ J_1 & 1 & 1 & 0 \\ & \sigma''' & \sigma & \sigma'' \end{matrix} \right] \right\} \tag{55}$$

$$Y_r^\sigma = \frac{1}{2} \frac{\hbar k_D}{k_B T} \sum_{\sigma'\sigma''} \left[\begin{matrix} r & 0 & 0 \\ J_2 & 1 & 0 & 0 \\ & \sigma & \sigma' & \sigma'' \end{matrix} + \begin{matrix} 0 & r & 0 \\ J_2 & 0 & 1 & 0 \\ & \sigma'' & \sigma & \sigma' \end{matrix} - \begin{matrix} 0 & 0 & r \\ J_2 & 0 & 0 & 1 \\ & \sigma' & \sigma'' & \sigma \end{matrix} \right]$$

$$\Gamma_\nu = \sum_\epsilon \sum_{\sigma'\sigma''} (\Gamma^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''} + \Gamma^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''})$$

$$Q_{r'\nu}^{\sigma'} = (\cos\chi) q_{r'x\sigma}^{\sigma'} \qquad S_{rr'}^{\sigma\sigma'} = N_0 \sum_{\sigma''} \int_0^1 q_{rx\sigma''}^{\sigma} q_{r'x\sigma''}^{\sigma'} x^2 \, dx$$

where

$$q_{r'x\sigma}^{\sigma'} = \sum_\epsilon \sum_{\sigma''\sigma'''} [x^{r'} \delta_{\sigma\sigma'} (\Gamma^{(1)}_{\sigma,\sigma'''\leftrightarrow\sigma''} + \Gamma^{(2)}_{\sigma\leftrightarrow\sigma''',\sigma''})$$
$$- (\delta_{\sigma'\sigma''} I^{(1)}_{\sigma,\sigma'''\leftrightarrow\sigma''} + \delta_{\sigma'\sigma'''} I^{(2)}_{\sigma\leftrightarrow\sigma''',\sigma''} - \delta_{\sigma'\sigma'''} I^{(3)}_{\sigma,\sigma'''\leftrightarrow\sigma''})]. \tag{56}$$

The coefficients that appear on the right-hand sides of equations (55) and (56) are given in the appendix.

The best set of adjustable parameters can be calculated from equation (21) and the corresponding first modified lower bound can consequently be obtained from equations (12*a*), (24) and (42). The analogous expressions after including the effect of other phonon processes will be given in the following section.

5. Other types of phonon interactions

In section 4 the calculations have been restricted to the case of three-phonon normal and Umklapp interactions. In the present section the effect of other types of phonon interactions, which play a significant role at low and intermediate temperatures, will be included. These types are boundary scattering, dislocation scattering and interactions with mass defects. The collision operator $\hat{H}$ can be expressed in the form

$$\hat{H} = \hat{H}_{3p} + \hat{H}_s \tag{57}$$

where $\hat{H}_s$ is the part of $\hat{H}$ that represents phonon interactions other than normal and Umklapp processes. The simplest form of $\hat{H}_s$ is that obtained by using the relaxation-time approximation, according to which

$$(\hat{H}_s\phi)_\nu = \Gamma_{\nu s}\phi_\nu \qquad \Gamma_{\nu s} = g_\nu \tau_{\nu s}^{-1} \qquad \tau_{\nu s}^{-1} = \tau_{\nu b}^{-1} + \tau_{\nu d}^{-1} + \tau_{\nu m}^{-1}. \tag{58}$$

Here $\tau_{\nu b}$, $\tau_{\nu d}$ and $\tau_{\nu m}$ are the relaxation times of boundary, dislocation and mass-defect scattering, which are given by [22–24]

$$\begin{aligned} &\tau_{\nu b}^{-1} = v_\sigma/L \qquad \tau_{\nu d}^{-1} = \tilde{\delta} y_\nu T \qquad \tau_{\nu m}^{-1} = \tilde{A}\omega_\nu^4 = \tilde{\alpha} y_\nu^4 T^4 \\ &\tilde{A} = \Omega\tilde{\Gamma}/(4\pi v^3) \qquad \tilde{\alpha} = (k_B/\hbar)^4 \tilde{A} \\ &3/v^3 = 2/v_t^3 + 1/v_\ell^3 \qquad y_\nu = \hbar v_\sigma k/k_B T. \end{aligned} \tag{59}$$

L is the specimen dimension, and $\tilde{\delta}$ and $\tilde{\Gamma}$ are the dislocation and mass-defect parameters. Equations (57) and (58) together with (4*b*) yield

$$H_{\nu\nu'} = (H_{3p})_{\nu\nu'} + \Gamma_{\nu s}\delta_{\nu\nu'}. \tag{60}$$

As regards mass defects, they can be represented more accurately by the complete form of the collision operator, which is given by

$$(\hat{H}_m\phi)_\nu = \sum_{\nu'} \bar{P}_\nu^{\nu'}(\phi_\nu - \phi_{\nu'}) = \Gamma_{\nu m}\phi_\nu - \sum_{\nu'} \bar{P}_\nu^{\nu'}\phi_{\nu'} = \sum_{\nu'} (H_m)_{\nu\nu'}\phi_{\nu'} \tag{61a}$$

where

$$(H_m)_{\nu\nu'} = \sum_{\nu''} \bar{P}_\nu^{\nu''}\delta_{\nu\nu'} - \bar{P}_\nu^{\nu'} \qquad \Gamma_{\nu m} = \sum_{\nu'} \bar{P}_\nu^{\nu'} \tag{61b}$$

and

$$\begin{aligned} &\bar{P}_\nu^{\nu'} = (P_\nu^{\nu'})_{N_\nu = \bar{N}_\nu} \qquad P_\nu^{\nu'} = W_\nu^{\nu'} N_\nu (N_{\nu'} + 1) \\ &W_\nu^{\nu'} = (\pi\tilde{\Gamma}/2N_0)\omega_\nu\omega_{\nu'}(e_\nu \cdot e_{\nu'})^2 \delta(\omega_{\nu'} - \omega_\nu). \end{aligned} \tag{61c}$$

Here e_ν is the polarization vector corresponding to the mode $\nu \equiv (\sigma, k)$ and $\Gamma_{\nu m}$ is the diagonal part of $\hat{H}_m$, which is related to $\tau_{\nu m}^{-1}$ by $\Gamma_{\nu m} = g_\nu \tau_{\nu m}^{-1}$. It is readily shown that this relation gives

$$(\tau_m^{-1})_{xt} = \tfrac{1}{2}\pi\tilde{\Gamma} k_D v_t (2 + c^3) x^4 \tag{62a}$$

and

$$(\tau_{\mathrm{m}}^{-1})_{x\ell} = \tfrac{1}{2}\pi\tilde{\Gamma}k_{\mathrm{D}}v_{\ell}\{1 + 2c^{-3}[1 - \theta(x-c)]\}x^4 \tag{62b}$$

where $c = v_t/v_\ell$ and $\theta(x-c)$ is the step function. If the term $\theta(x-c)$ is neglected in (62*b*), then (62*a*) and (62*b*) can be combined to give the same expression for $\tau_{\nu\mathrm{m}}$ as that given in equation (59). The neglect of the term $\theta(x-c)$ is justified for $T \ll \theta_{\mathrm{D}}$ where θ_{D} is the Debye temperature.

The most direct decompositions of the operator $\hat{H}$, which are analogous to (51*a*), yield the following expressions for the operator $\hat{J}$:

$$(\hat{J}\psi)_\nu = J_{\nu i}\psi_\nu \qquad i = 0, 1, 2 \text{ for any } \psi \tag{63a}$$

where

$$\begin{aligned} J_{\nu i} &= B_i + \tfrac{1}{2}i(i-1)\Gamma_{\nu\mathrm{s}} \\ B_i &= \{3\Gamma_\nu + (2-i)[\Gamma_{\nu\mathrm{m}} + \tfrac{1}{2}(i+1)(\Gamma_\nu)_{\mathrm{bd}}]\}_{\max} \qquad i = 0, 1, 2 \end{aligned} \tag{63b}$$

and

$$\begin{aligned} (\Gamma_\nu)_{\mathrm{bd}} &= g_\nu(\tau_\nu^{-1})_{\mathrm{bd}} = g_\nu(\tau_{\nu\mathrm{b}}^{-1} + \tau_{\nu\mathrm{d}}^{-1}) \\ \Gamma_{\nu\mathrm{s}} &= \Gamma_{\nu\mathrm{m}} + (\Gamma_\nu)_{\mathrm{bd}} = g_\nu[\tau_{\nu\mathrm{m}}^{-1} + (\tau_\nu^{-1})_{\mathrm{bd}}]. \end{aligned} \tag{63c}$$

Other possible decompositions are discarded according to the findings of section 3. In the decompositions $i = 1, 2$, $\hat{H}_{\mathrm{s}}$ is defined from equations (58)–(60). For $i = 1$ the Perron–Frobenius theorem is applied to the total operator $\hat{H}$, while for $i = 2$ the theorem is applied to $\hat{H}_{3\mathrm{p}}$. The decomposition $i = 0$ is obtained by applying the Perron–Frobenius theorem to the total operator $\hat{H}$ with $\hat{H}_{\mathrm{m}}$ defined by (61*a*, *b*) and with $\phi_{\tilde{\nu}} = -\phi_\nu$, where $\tilde{\nu} = (\sigma, \tilde{k})$, $\tilde{k} = (k_1, k_2, -k_3)$ and k_3 is the component of k along $\nabla T \cdot \Gamma_{\nu\mathrm{m}}$ and $\tau_{\nu\mathrm{m}}^{-1}$ are accordingly defined from (62*a*, *b*).

It was further found that all the terms that arise from the off-diagonal part of $\hat{H}_{\mathrm{m}}$ will vanish identically. Consequently, for the three decompositions presented by (63*a*) we have

$$\begin{aligned} \langle\psi, \hat{H}\hat{J}^{-1}X\rangle &= u^2\gamma^{-1}\sum_{\sigma r} a_r^\sigma(Y_{ri}^\sigma + R_{ri}^\sigma) \\ \langle\psi, \hat{H}\psi\rangle &= u^2\sum_{\substack{\sigma\sigma' \\ rr'}} a_r^\sigma a_{r'}^{\sigma'}(H_{rr'}^{\sigma\sigma'} + E_{rr'}^{\sigma\sigma'}) \\ \langle\psi, \hat{H}\hat{J}^{-1}\hat{H}\psi\rangle &= u^2\gamma^{-1}\sum_{\substack{\sigma\sigma' \\ rr'}} a_r^\sigma a_{r'}^{\sigma'}[(S_{rr'}^{\sigma\sigma'})_i + (U_{rr'}^{\sigma\sigma'})_i + (D_{rr'}^{\sigma\sigma'})_i] \\ \langle X, \hat{J}^{-1}X\rangle &= u^2\gamma^{-1}X_i \qquad \gamma = 3\pi\hbar k_{\mathrm{D}}^2/(8\rho\Omega). \end{aligned} \tag{64}$$

The quantity Y_{ri}^σ takes the same form as the quantity Y_r^σ (equations (53) and (55)) but with Y_ν being replaced by

$$Y_{\nu i} = v_\sigma^2 x g_\nu \bar{J}_{\nu i}^{-1} \qquad \bar{J}_{\nu i} = \gamma^{-1}J_{\nu i}. \tag{65}$$

The two coefficients J_2 and $F_2^{mm'm''}$ (equations (55) and (A1*a*, *b*)) will accordingly be replaced by J_{2i} and $F_{2i}^{mm'm''}$ due to the replacement of Y_ν, $Y_{\nu'}$, $Y_{\nu''}$ by $Y_{\nu i}$, $Y_{\nu' i}$, $Y_{\nu'' i}$. Also,

$$X_i = N_0 \left(\frac{\hbar k_D}{k_B T}\right)^2 \sum_\sigma v_\sigma^4 \int_0^1 x^4 g_\nu^2 \bar{J}_{\nu i}^{-1}\, dx$$

$$R_{ri}^\alpha = \frac{\gamma N_0 \hbar k_D}{k_B T} v_\sigma^2 \int_0^1 x^{r+3} g_\nu^2 \bar{\tau}_{\nu s}^{-1} \bar{J}_{\nu i}^{-1}\, dx \qquad \bar{\tau}_{\nu s} = \gamma \tau_{\nu s}$$

$$E_{rr'}^{\sigma\sigma'} = \gamma N_0 \delta_{\sigma\sigma'} \int_0^1 x^{r+r'+2} g_\nu \bar{\tau}_{\nu s}^{-1}\, dx \tag{66}$$

$$(S_{rr'}^{\sigma\sigma'})_i = N_0 \sum_{\sigma''} \int_0^1 \bar{J}_{x\sigma'' i}^{-1} q_{rx\sigma''}^\sigma q_{r'x\sigma''}^{\sigma'} x^2\, dx$$

$$(D_{rr'}^{\sigma\sigma'})_i = \gamma^2 N_0 \delta_{\sigma\sigma'} \int_0^1 x^{r+r'+2} (g_\nu \bar{\tau}_{\nu s}^{-1})^2 \bar{J}_{\nu i}^{-1}\, dx.$$

Moreover, the expression for $(U_{rr'}^{\sigma\sigma'})_i$ can be obtained from the expression for $H_{rr'}^{\sigma\sigma'}$ (equation (55)) by replacing the coefficient J_1 by the coefficient I_i, which is given in the appendix (equation (A5)).

The best set of adjustable parameters and the first modified lower bound are accordingly determined by

$$\bar{Z}_{ri}^\sigma = \sum_{\sigma' r'} (\bar{G}_{rr'}^{\sigma\sigma'})_i \bar{a}_{r'}^{\sigma'} \tag{67*a*}$$

$$\kappa_1^<(J_{\nu i}, \psi_\nu) = \frac{8\rho\hbar}{3\pi k_B T^2} \left(\sum_{\substack{\sigma\sigma' \\ rr'}} \bar{Z}_{ri}^\sigma (\bar{G}_i^{-1})_{rr'}^{\sigma\sigma'} \bar{Z}_{r'i}^{\sigma'} + \bar{X}_i \right) \tag{67*b*}$$

where

$$\bar{a}_r^\sigma = \gamma \left(\frac{k_B T}{\hbar k_D}\right) a_r^\sigma \qquad \bar{X}_i = \frac{1}{N_0} \left(\frac{k_B T}{\hbar k_D}\right)^2 X_i$$

$$\bar{Z}_{ri}^\sigma = \frac{1}{N_0} \left(\frac{k_B T}{\hbar k_D}\right) [X_r^\sigma - \gamma^{-1}(Y_{ri}^\sigma + R_{ri}^\sigma)] \tag{68}$$

$$(\bar{G}_{rr'}^{\sigma\sigma'})_i = (1/\gamma N_0)\{H_{rr'}^{\sigma\sigma'} + E_{rr'}^{\sigma\sigma'} - \gamma^{-1}[(S_{rr'}^{\sigma\sigma'})_i + (U_{rr'}^{\sigma\sigma'})_i + (D_{rr'}^{\sigma\sigma'})_i]\}.$$

The general expressions for $\psi_\nu = \boldsymbol{u} \cdot \boldsymbol{k}$ (one variational parameter) can be retrieved from (12*a*) and (38) with $\theta_{1k} = -ux\cos\chi$. It can be shown after some manipulation that

$$\kappa_1^<(J_{\nu i}, \psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k}) = \frac{8\rho\hbar}{3\pi k_B T^2} \Bigg[\Bigg(\sum_\sigma v_\sigma^2 [II_\sigma^{(1)} - (II_\sigma^{(1)})_i] - v_\ell^2 \sum_{\sigma\sigma'\sigma''} (II_{\sigma,\sigma'\leftrightarrow\sigma''}^{(1)})_i \Bigg)^2$$

$$\times \Bigg(2 \sum_{\sigma\sigma'\sigma''} [II_{\sigma,\sigma'\leftrightarrow\sigma''}^{(1)} - (II_{\sigma,\sigma'\leftrightarrow\sigma''}^{(2)})_i]$$

$$+ \sum_\sigma [II_\sigma^{(2)} - (II_\sigma^{(2)})_i - (II_\sigma^{(3)})_i] \Bigg)^{-1} + \bar{X}_i \Bigg] \qquad i = 0, 1, 2 \tag{69}$$

where

$$II_\sigma^{(j)} = \int_0^1 x^4 g_\nu \bar{\tau}_{\nu s}^{(1-j)}\,dx \qquad (II_\sigma^{(j)})_i = \int_0^1 x^4 g_\nu^2 \bar{J}_{\nu i}^{-1} \bar{\tau}_{\nu s}^{-j}\,dx \qquad j = 1, 2$$
$$(II_\sigma^{(3)})_i = \int_0^1 x^2 \bar{J}_{\nu i}^{-1} \left(\sum_{\sigma'\sigma''} M^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''} + \sum_{\sigma'\sigma''} M^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''} \right)^2 dx. \tag{70}$$

The expressions for $M^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''}$ and $M^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''}$ were obtained in Mikhail [12]. They are given here in the appendix together with the expressions for the other coefficients involved in equation (69).

6. Experimental applications

In the previous two sections the basic equations and formulae needed for the calculation of the first modified lower bound on the phonon thermal conductivity have been derived. The variational trial function depended on a series of variational parameters. The simple case of one variational parameter has been deduced as a special result. In this section the expressions obtained are used to evaluate the thermal conductivity of germanium and lithium fluoride. The input data needed for the calculations are taken from Hamilton and Parrott [3], Srivastava [25] and table 1 of Mikhail and Madkour [14]. The corresponding experimental results were given in Geballe and Hull [26] for Ge and in Berman and Brock [27] for LiF.

6.1. Details of numerical calculations

The integrals involved in the calculations are evaluated numerically to a sufficiently high accuracy by using the Gaussian quadrature method with 24 pivots. The values of the variational parameters a_r^σ ($r = 1, 2, \ldots, r_{\max}$; $\sigma = t, \ell$) are obtained by inverting numerically the matrix $\{G_{rr'}^{\sigma\sigma'}\}$. The value of $r_{\max}$ is allowed to vary from 1 to 7. The variational procedure is therefore carried out in successive steps. In each step $r_{\max}$ is increased by one and thus two additional variational parameters are included ($\sigma = t, \ell$). The calculations are terminated if either the difference between the values of the thermal conductivity calculated in two successive steps is less than 1% or $r_{\max}$ exceeds 7.

6.2. Results and discussion

The first modified lower bound on the thermal conductivity for Ge and LiF has been calculated numerically from equation (67*b*). In the special case of one variational parameter ($\psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k}$), equation (69) has been used instead. We now proceed to consider the following four points:

(i) In Srivastava [9] the first modified lower bound on the thermal conductivity of Ge was calculated by using the simple trial function $\psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k}$. Srivastava [9] considered only three-phonon interactions and used a very simple approximate form for the tensor $A_{\nu\nu'\nu''}$. He further performed the calculations in the high temperature range ($T \geqslant 300$ K) where the leading terms only were retained. Besides, the areas of integrations for the three-phonon processes $\nu \leftrightarrow \nu' + \nu''$ (specified by (50*b*)) used in [9] were later amended in [14]. Also, the reciprocal lattice vector for the Umklapp processes of this type was taken in [9] in a different form from that given in (50*b*). It was argued in [14] that the form given in (50*b*) is

a more reasonable choice. In view of these considerations we used equation (69) to calculate $\kappa_1^<(\beta, \psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k})$ for Ge when three-phonon interactions only are taken into consideration. The form of the reciprocal lattice vector given in (50*b*) is thus used instead of the form used in [9]. The general expressions for $A_{\nu\nu'\nu''}$ together with the correct areas of integrations were also utilized. We started the calculations at $T = 50$ K, around which normal processes start to dominate the phonon scattering mechanism and the solution $\psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k}$ becomes valid. The calculations were extended to the high temperature range to compare the results with those of Srivastava [9]. The results obtained in this range are given in table 1 together with the corresponding results from [9]. The present modifications have improved the results since the value of $\kappa_1^<$ has been increased for $T = 300$–900 K. It has been increased by a factor of 3.2 at $T = 300$ K. The factor decreases with the increase of temperature until it became 2.83 at $T = 900$ K.

Table 1. Comparison between the values of $\kappa_1^<(\beta, \psi_\nu = \boldsymbol{u}\cdot\boldsymbol{k})$ obtained in the present work and those obtained in Srivastava [9].

	$\kappa_1^<$ (W cm^{-1} K^{-1})	
T (K)	Present work	Srivastava [9]
300	1.15	0.355
500	0.692	0.231
700	0.496	0.171
900	0.386	0.136

(ii) The results of the first modified lower bound obtained from equation (67*b*) by using a power-series trial function are displayed in figure 1 for the natural and enriched specimens of Ge of Geballe and Hull [26] and in figure 2 for two of the specimens of LiF (labelled by 6 and 8 in table 1 of Berman and Brock [27]). The corresponding results obtained by considering normal and Umklapp processes alone are also given for the two materials in the same figures. The experimental data of [26] for Ge are shown in figure 1 while the measurements of [27] for LiF are presented in figure 2. The theoretical results for the two specimens of Ge were calculated by using the three forms of the operator $\hat{J}$ (of the quantities $J_{\nu i}$, B_i, $i = 0, 1, 2$) given in (63). The differences between the three sets of results were found to be insignificant within the accuracy of the computations. For the enriched specimen the differences never exceed 0.4%. Also, an excellent convergence was found over the whole temperature range for the three sets of results as r_{max} increases. As regards the natural specimen, we have generally used the results of $i = 0$ in which the exact collision operator of mass defects is considered and accordingly the mass-defect relaxation time is defined by (62*a*, *b*). However, for this specimen the convergence was found to be weak over the temperature range $T = 16$–40 K when r_{max} increases from 5 to 7. Over this temperature range we compared the results of the three sets to choose the best value (the dashed-double dotted part of the lower full curve in figure 1). We believe that the convergence for this specimen over this temperature range may be improved if the calculations are carried out on a computer of better accuracy. For the two specimens of LiF the results were obtained by using the expressions for $i = 0$ in (63) and were found to converge quite reasonably over the whole temperature range as r_{max} increases. Also, an excellent convergence was found for both Ge and LiF at all temperatures in the case when three-phonon normal and Umklapp processes occur alone. Moreover, the agreement between the theoretical and experimental

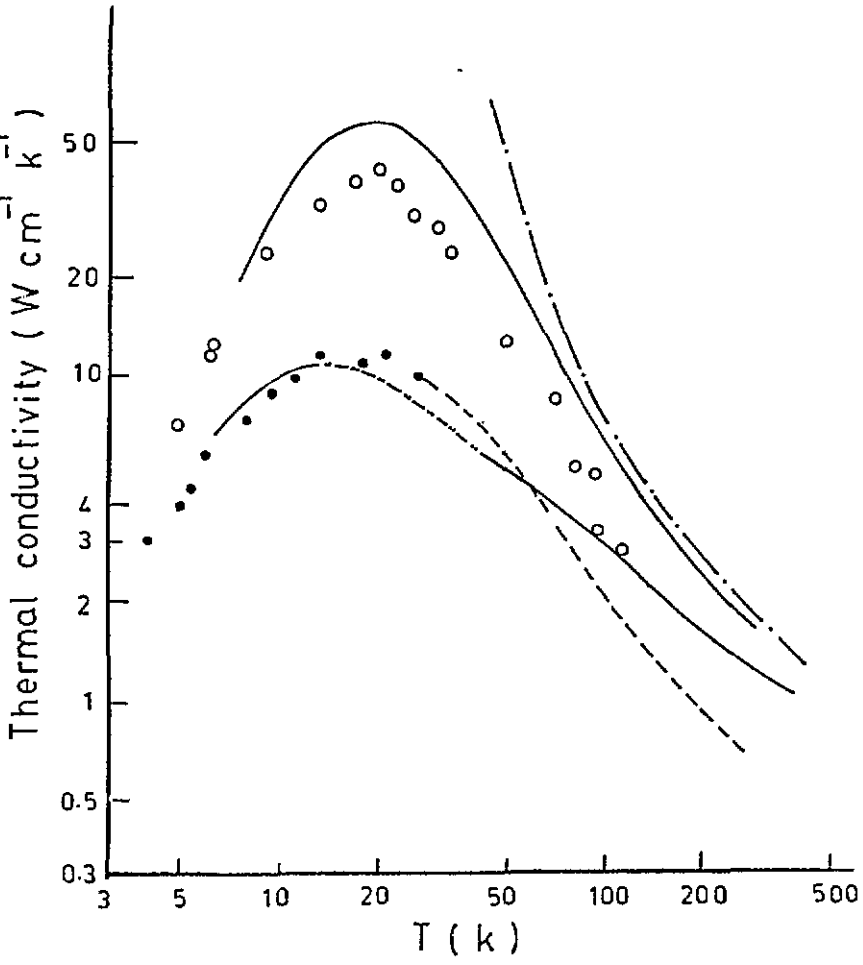

Figure 1. Graph of thermal conductivity against temperature for Ge. The lower (natural specimen) and upper (enriched specimen) full curves and the dashed–double dotted part of the lower curve refer to the results obtained for the first modified lower bound by using a power-series trial function (equation (67*b*)). The corresponding experimental results of Geballe and Hull [26] are represented by the full circles and the broken curve (natural specimen) and by the open circles (enriched specimen). The dashed–dotted curve represents the results calculated with a power-series trial function when three-phonon interactions occur alone.

results is quite reasonable for both materials bearing in mind that no fitting parameters are used.

It should, however, be noted that in the case of the enriched specimen and a part of the results of the natural specimen of Ge and for the two specimens of LiF the theoretical results of the first modified lower bound are greater than the experimental values. The same behaviour was also noticed regarding the results obtained from the ordinary variational principle for Ge [3]. This may be attributed to the use of the continuum model and the neglect of dispersion, which increase the group velocity of acoustic phonons and accordingly the calculated heat current and thermal conductivity. Also, the crystals of Ge and LiF are cubic with two atoms per unit cell. The dispersion relation of these materials consists of three acoustic as well as three optical branches. In order to counterbalance the neglect of the

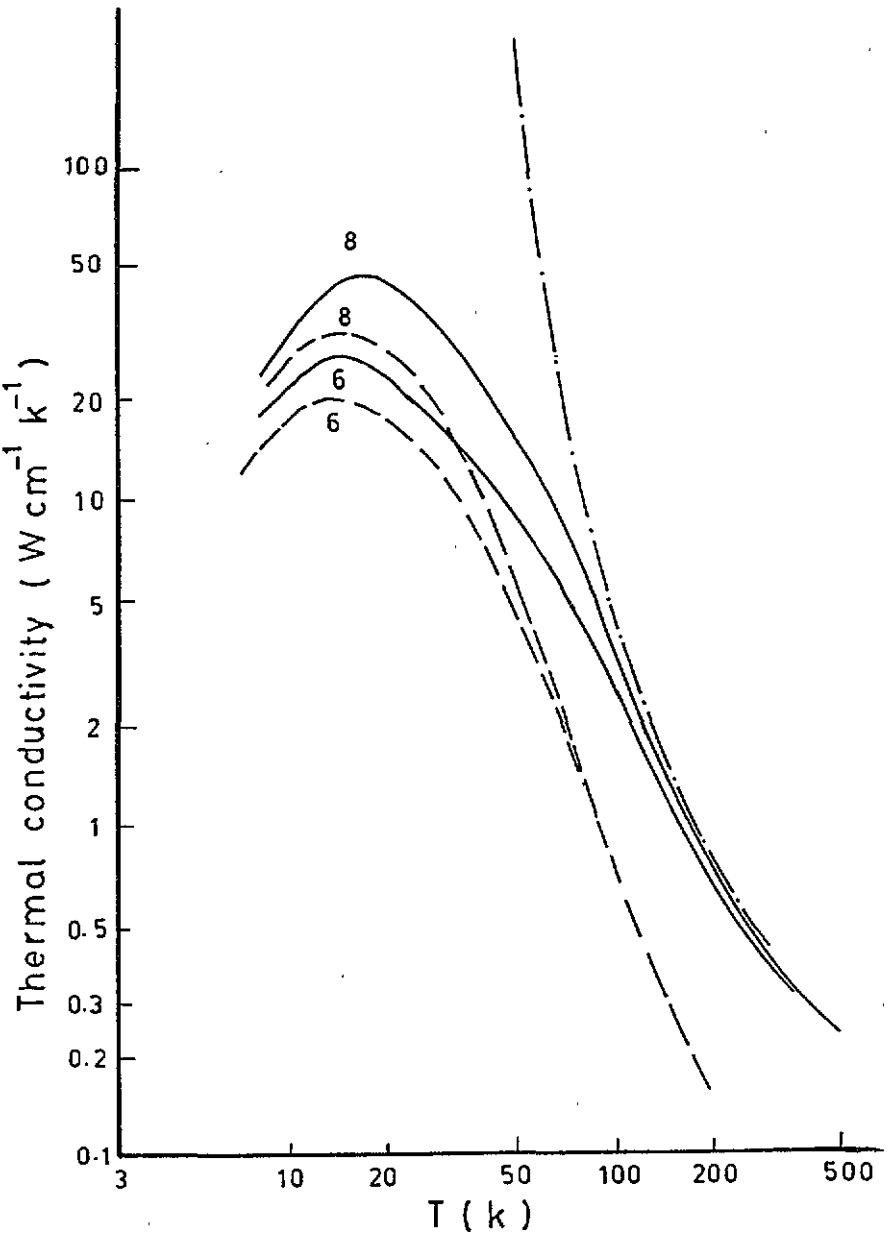

Figure 2. *A plot of thermal conductivity versus temperature for LiF. The full curves refer to the* results obtained for the first modified lower bound by using a power-series trial function, while the broken curves refer to the corresponding experimental values. The specimens are labelled by the same numbers as in Berman and Brock [27]. The dashed–dotted curve represents the results calculated with a power-series trial function when three-phonon interactions occur alone.

optical branches, an extended zone scheme has been used for the acoustic branches. This overestimates the effect of optical branches since the group velocity is taken throughout to be the velocity of sound. Moreover, the isotropic model used for Umklapp processes restricts

this type of interaction to be coplanar. The neglect of the three-dimensional nature of Umklapp processes may lead to an increase in the calculated values of thermal conductivity.

(iii) In figure 3, a comparison is made for the enriched specimen of Ge between the results obtained for the first modified lower bound by using the $u \cdot k$ trial function (equation (69)) and by using a power-series trial function (equation (67*b*)) with $r_{max} = 1$–6. The figure demonstrates further how the results converge and approach the exact value when r_{max} increases and the number of variational parameters increases accordingly.

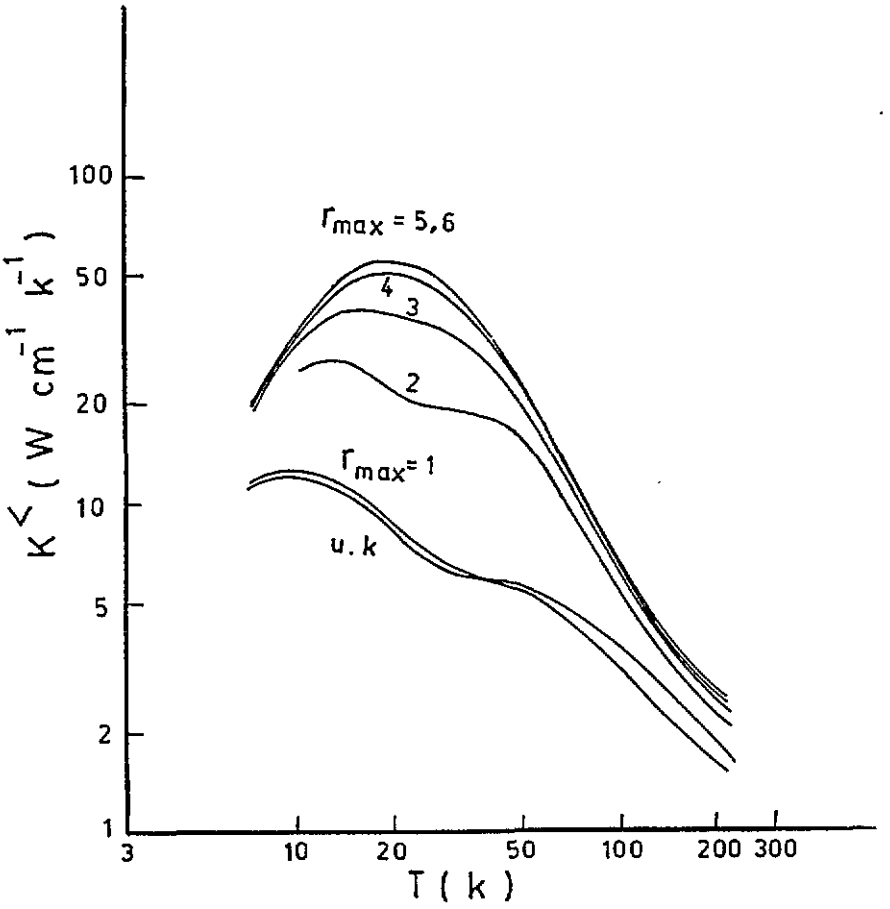

Figure 3. Graph of the first modified lower bound against temperature for the enriched specimen of Ge. The results are obtained by using the $u \cdot k$ trial function (equation (69)) and by using a power-series trial function (equation (67*b*)) with $r_{max} = 1$–6.

(iv) In principle, the convergence of the calculations of the first modified lower bound (present treatment) must converge much faster than the ordinary lower bound [3] as r_{max} increases. In order to investigate this point, we have calculated the ordinary lower bound for Ge and LiF in the case when normal and Umklapp processes exist alone. It was found that up to $r_{max} = 4$ the first modified lower bound is always higher than the ordinary lower bound and is thus nearer to the exact analytical value. The difference decreases as r_{max} increases but the calculations have to be carried out to a very high accuracy to investigate whether the two sets converge to the same limit or to different limits.

7. Conclusions

The complementary variational principle has been used successfully to determine the general expressions required for the calculation of the first modified lower and upper bounds as well as the relations needed to select the best decomposition of the collision operator for each type of bound. The present modifications for the calculation of the first modified lower bound have considerably improved the results of earlier treatments. The numerical results obtained for the phonon thermal conductivity by using this bound and a variational trial function that depends on a series of variational parameters showed a good quantitative agreement with the experimental data of Ge and LiF. The results showed also a reasonable convergence when the number of variational parameters increases. The convergence was further proved analytically.

Appendix. Basic coefficients and integrals

In this appendix we give the required expressions for the basic coefficients used in sections 4 and 5. They are all expressed in terms of double integrals over x and x' or single integrals over x' for a given x in the interval $(0, 1)$. Also, all the integrals depend on the tensor $A_{\nu\nu'\nu''}$, which measures the strength of three-phonon interactions. The areas and limits of integrations and the expressions for $A_{\nu\nu'\nu''}$ were given in Hamilton and Parrott [3] and Srivastava *et al* [28] for the processes $\nu + \nu' \leftrightarrow \nu''$ (described by 50*a*)) and in Mikhail and Madkour [14] for the processes $\nu \leftrightarrow \nu' + \nu''$ (described by (50*b*)).

The coefficients involved in equations (55) and (56) are given by

$$J_{j\ m\ m'\ m''}^{\ r\ r'\ r''} = \frac{\gamma N_0}{\alpha\alpha'} \sum_{\epsilon} \int\int x^{r+2} x'^{r'+2} (\alpha x + \alpha' x')^{r''+1} \times [1 - \epsilon + \epsilon(\alpha x + \alpha' x')] \frac{\mathcal{F}_{\nu\nu'}^{\nu''}}{(\lambda + 2\mu)^2} \epsilon^{m''} F_j^{mm'm''} \, dx \, dx' \qquad j = 1, 2 \quad \text{(A1}a\text{)}$$

$$F_j^{mm'm''} = \frac{3}{4\pi} \int_0^{\pi} \int_0^{2\pi} (\sin\chi \cos^m \chi \cos^{m'} \chi' \cos^{m''} \eta) \times (Y_{x\sigma} \cos\chi + Y_{x'\sigma'} \cos\chi' - \epsilon Y_{x''\sigma''} \cos\eta)^{j-1} \, d\chi \, d\phi' \qquad j = 1, 2 \quad \text{(A1}b\text{)}$$

$$\Gamma_{\sigma,\sigma'\leftrightarrow\sigma''}^{(1)} = \frac{\gamma}{\alpha\alpha'} \int x'^2 (\alpha x + \alpha' x')[1 - \epsilon + \epsilon(\alpha x + \alpha' x')] \frac{\mathcal{F}_{\nu\nu'}^{\nu''}}{(\lambda + 2\mu)^2} \, dx'$$

$$\Gamma_{\sigma\leftrightarrow\sigma',\sigma''}^{(2)} = \frac{\gamma\alpha^3}{\alpha'} \frac{x}{2(1 - \epsilon + \epsilon x)} \int x'^2 (\alpha x - \alpha' x')^2 \frac{\mathcal{F}_{\nu'\nu''}^{\nu}}{(\lambda + 2\mu)^2} \, dx' \qquad \text{(A2)}$$

$$I_{\sigma,\sigma'\leftrightarrow\sigma''}^{(1)} = \frac{\epsilon\gamma}{\alpha\alpha'} \int x'^2 (\alpha x + \alpha' x')^{r'+1} (x + x' C') \frac{\mathcal{F}_{\nu\nu'}^{\nu''}}{(\lambda + 2\mu)^2} \, dx'$$

$$I_{\sigma\leftrightarrow\sigma',\sigma''}^{(2)} = \frac{\gamma\alpha^3}{\alpha'} \frac{x}{(1 - \epsilon + \epsilon x)} \int \tilde{C}' x'^{r'+2} (\alpha x - \alpha' x')^2 \frac{\mathcal{F}_{\nu'\nu''}^{\nu}}{(\lambda + 2\mu)^2} \, dx' \qquad \text{(A3)}$$

$$I_{\sigma,\sigma'\leftrightarrow\sigma''}^{(3)} = \frac{\gamma}{\alpha\alpha'} \int C' x'^{r'+2} (\alpha x + \alpha' x')[1 - \epsilon + \epsilon(\alpha x + \alpha' x')] \frac{\mathcal{F}_{\nu\nu'}^{\nu''}}{(\lambda + 2\mu)^2} \, dx'$$

where γ is defined by equation (64) and

$$\alpha = v_\sigma / v_{\sigma''} \qquad \alpha' = v_{\sigma'} / v_{\sigma''} \qquad \mathcal{F}^{\nu''}_{\nu\nu'} = |A_{\nu\nu'\nu''}|^2 \bar{N}_\nu \bar{N}_{\nu'} (\bar{N}_{\nu''} + 1)$$

$$C' = \cos\theta' = \frac{(\alpha x + \alpha' x' - 1 + \epsilon)^2 - x^2 - x'^2}{2xx'} \quad \text{(for the process } \nu + \nu' \leftrightarrow \nu'') \tag{A4}$$

$$\tilde{C}' = \cos\theta' = \frac{(\alpha x - \alpha' x')^2 - x'^2 - (1 - \epsilon - x)^2}{2x'(1 - \epsilon - x)} \quad \text{(for the process } \nu \leftrightarrow \nu' + \nu'').$$

Here (θ', ϕ') are the polar and azimuthal angles in the x' space, where the polar axis is taken in the direction of x and thus θ' is the angle between x and x' while ϕ' is measured from the plane consisting of x and ∇T. Also, η is the angle between $x + x'$ and ∇T ($\cos\chi'' = \epsilon\cos\eta$). The dependence of $F_j^{mm'm''}$ on $\sigma, \sigma', \sigma''$ and on x, x' as well as the dependence of $\Gamma^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''}$, $\Gamma^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''}$ on x, ϵ and the dependence of $I^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''}$, $I^{(3)}_{\sigma,\sigma'\leftrightarrow\sigma''}$, $I^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''}$ on x, ϵ, r are dropped for simplicity.

Also, the coefficient I_i needed for the calculation of $(U^{\sigma\sigma'}_{rr'})_i$ (equation (64)) is given by

$$I_i \begin{matrix} r & r' & r'' \\ m & m' & m'' \\ \sigma & \sigma' & \sigma'' \end{matrix} = \frac{\gamma^2 N_0}{\alpha\alpha'} \sum_\epsilon \iint x^{r+2} x'^{r'+2} (\alpha x + \alpha' x')^{r''+1} [1 - \epsilon + \epsilon(\alpha x + \alpha' x')]$$

$$\times (m g_\nu \bar{\tau}^{-1}_{\nu s} \bar{J}^{-1}_{\nu i} + m' g_{\nu'} \bar{\tau}^{-1}_{\nu' s} \bar{J}^{-1}_{\nu' i} + m'' g_{\nu''} \bar{\tau}^{-1}_{\nu'' s} \bar{J}^{-1}_{\nu'' i}) \frac{\mathcal{F}^{\nu''}_{\nu\nu'}}{(\lambda + 2\mu)^2} \epsilon^{m''} F_1^{mm'm''} \, dx \, dx'. \tag{A5}$$

Finally, the coefficients involved in equations (69) and (70) can be expressed as

$$II^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''} = \frac{1}{\alpha\alpha'} \left(\iint x^2 x'^2 (\alpha x + \alpha' x')(2 - \alpha x - \alpha' x') \frac{\mathcal{F}^{\nu''}_{\nu\nu'}}{(\lambda + 2\mu)^2} \, dx \, dx' \right)_U \tag{A6}$$

$$(II^{(U)}_{\sigma,\sigma'\leftrightarrow\sigma''})_i = \frac{1}{\alpha\alpha'} \left(\iint x^2 x'^2 (\alpha x + \alpha' x') \frac{\mathcal{F}^{\nu''}_{\nu\nu'}}{(\lambda + 2\mu)^2} \right.$$

$$\times [x(x + x'C') g_\nu \bar{J}^{-1}_{\nu i} \bar{\tau}^{(1-j)}_{\nu s} \alpha^{2(2-j)} + x'(x' + xC') g_{\nu'} \bar{J}^{-1}_{\nu' i} \bar{\tau}^{(1-j)}_{\nu' s} \alpha'^{2(2-j)}$$

$$\left. + (\alpha x + \alpha' x')(2 - \alpha x - \alpha' x') g_{\nu''} \bar{J}^{-1}_{\nu'' i} \bar{\tau}^{(1-j)}_{\nu'' s}] \, dx \, dx' \right)_U \qquad j = 1, 2 \tag{A7}$$

and

$$M^{(1)}_{\sigma,\sigma'\leftrightarrow\sigma''} = \frac{2}{\alpha\alpha'} \left(\int x'^2 (\alpha x + \alpha' x')(x + x'C') \frac{\mathcal{F}^{\nu''}_{\nu\nu'}}{(\lambda + 2\mu)^2} \, dx' \right)_U$$

$$M^{(2)}_{\sigma\leftrightarrow\sigma',\sigma''} = \frac{\alpha^3}{\alpha'} \frac{x}{2 - x} \left(\int x'^2 (\alpha x - \alpha' x')^2 \frac{\mathcal{F}^{\nu}_{\nu'\nu''}}{(\lambda + 2\mu)^2} \, dx' \right)_U . \tag{A8}$$

The subscript U indicates that for three-phonon interactions the contribution due to normal processes vanishes and Umklapp processes only are considered.

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