Phonon Scattering by Lattice Defects. II*

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This paper treats several aspects of phonon scattering using the t-matrix–Green's function method. We first prove an optical theorem and establish the orthonormality of the solutions to the scattering problem for a quite general perturbation to the lattice. We then expand an earlier discussion of the representation of the t matrix in terms of the eigenvectors of the matrix $g\gamma$. Application of these results is then made to a "model defect," namely, a substitutional impurity in a diatomic lattice with a changed mass and a changed force constant to nearest neighbors. Expressions are derived, that are exact within the model, for the phonon scattering rate and relaxation time. These are in a form suitable for calculations using good "model phonons." A rigorous expression is also derived for the relaxation time for phonon scattering by isotopes in a diatomic crystal lattice.

I. INTRODUCTION

THE subject of phonon scattering by lattice defects was first treated by Lifshitz.[1] It has subsequently been discussed by many workers,[2–10] including the author.[11] In spite of these efforts, several important aspects of the problem still require clarification or more general treatment than has been given so far. Such is the subject of this paper, the aim of which is to carry derivations of formulas to the point where they can be directly applied to calculations of the scattering by simple, but not unrealistic, "model" defects of simple, but not unrealistic, "model" phonons. An example of model defects is given by substitutional monovalent impurities in a diatomic crystal, perturbing the lattice through a change in mass and a change in central force constant to nearest neighbors. Example model phonons are furnished by the phonon frequencies and eigenvectors obtained from calculations based on a shell model or deformation dipole model of an alkali halide lattice.

In Sec. II, we derive an optical theorem and prove the orthonormality of the solutions given in I of the scattering problem for a very general class of defects. Such theorems are well known from the quantum mechanical theory of scattering, but the proofs do not carry over directly to phonon scattering, because when changes in mass are involved, there is also a change in the "effective metric tensor." [See Eq. (2.3) below.] An optical theorem for phonon scattering has been discussed by Thoma and Ludwig[9] in a less general way than is done here. Similarly, the orthonormality of the solutions has been indicated by Gunther for the specific case of the mass defect approximation (MDA).[10]

In Sec. III, we examine some properties of the t matrix, the matrix that uniquely describes the scattering from a single defect. In Secs. IIIA and B we expand the discussion begun in I of the representation of t in terms of the eigenvectors of the matrix $g\gamma$ and show how consideration of the symmetry of the defect aids in this task. Callaway has used symmetry arguments in his treatment of scattering in crystals,[3] but his emphasis is somewhat different from ours. In Sec. IIIC, we apply our general methods to a specific model of a defect, namely, the one mentioned in the first paragraph of this introduction.

In Sec. IV, we apply these methods to phonon scattering by two kinds of defects: a strongly perturbing dilute impurity and isotopes. The phonon lifetime as limited by defect scattering is calculated in Sec. IV.A. The transition rates are calculated using the "golden rule." The optical theorem then yields the simple result of Eq. (4.16) for the lifetime.

The suitability of the phonon lifetime for thermal conductivity calculations is discussed in Sec. IVB. It has been widely recognized that in the MDA the lifetime can be used directly as a thermal conductivity relaxation time.[12,13] We point out that this use is more generally valid provided that a kind of interference between even and odd parity phonon scattering [Eq. (4.24)] can be neglected.

In Sec. IVC the earlier results are examined in the long-wavelength weak-coupling acoustical limit, and Rayleigh scattering is obtained. In the process we discover that care must sometimes be exercised in the choice of a basis for the t matrix so that the correct

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limiting behavior can be obtained in numerical calculations.

In Sec. IVD we discuss phonon scattering by isotopes in a diatomic crystal. The result is expressed in a form suitable for use with accurate models for the phonons.

We shall rely heavily on the contents of I and on the notation used there. A few changes in notation will be necessary and will be discussed as we proceed.

II. OPTICAL THEOREM AND ORTHONORMALITY OF SOLUTIONS

A. Introduction

The lattice dynamics problem of interest is a classical "small oscillation" problem—the simultaneous diagonalization of the perturbed potential-energy matrix $V+\Delta V$ and the perturbed mass matrix $M+\Delta M$.[14] The orthonormality condition for two eigenvectors, $u(l)$ and $u(l')$ of $V+\Delta V$, is usually written as

$$u(l')^\dagger(M+\Delta M)u(l)=\delta_{ll'}, \tag{2.1}$$

where the symbol † denotes the Hermitian conjugate. If we introduce new dynamical coordinates by

$$v=M^{1/2}u \tag{2.2}$$

[See Eq. (5) of I], Eq. (2.1) becomes

$$v(l')^\dagger(I+M^{-1}\Delta M)v(l)=\delta_{ll'}. \tag{2.3}$$

Here I denotes the unit matrix. We can assume that the phonon eigenvectors $v(k\lambda)$ or

$$v_{k\lambda}{}^j(\mathbf{L})=N^{-1/2}\epsilon_{k\lambda}{}^j e^{i\mathbf{k}\cdot\mathbf{L}}, \tag{2.4}$$

that diagonalize

$$A=M^{-1/2}VM^{-1/2},$$

satisfy

$$v(k'\lambda')^\dagger v(k\lambda)=\delta_{kk'}\delta_{\lambda\lambda'}. \tag{2.5}$$

The eigenvectors for the perturbed problem are given by combining Eqs. (19) and (24) of I. They arise in a well-defined way from the unperturbed eigenvectors $v(k\lambda)$ of Eq. (2.4); therefore they will be labeled $\hat{v}(k\lambda)$:

$$\hat{v}(k\lambda)=[I-G(\omega_{k\lambda}{}^2+i\epsilon)T(\omega_{k\lambda}{}^2+i\epsilon)]v(k\lambda), \tag{2.6}$$

where

$$G(z)\equiv(A-zI)^{-1}, \tag{2.7}$$

and $T(z)$ satisfies the equation [I, Eq. (24′)]

$$T(z)=\Gamma-T(z)G(z)\Gamma=\Gamma-\Gamma G(z)T(z). \tag{2.8}$$

The perturbed dynamical matrix will be of the form (we set the coupling constant "α" of I equal to one)

$$\Gamma=\Gamma_m+\Gamma_f, \tag{2.9}$$

where Γ_m is due to the change in mass

$$\Gamma_m=-(\Delta M)M^{-1}\omega^2, \tag{2.10}$$

and Γ_f is due to the change in potential-energy matrix:

$$\Gamma_f=M^{-1/2}(\Delta V)M^{-1/2}. \tag{2.11}$$

Because of Eq. (2.10) we must consider Γ to be a function of z in an equation like (2.8):

$$\Gamma(z)\equiv-(\Delta M)M^{-1}z+\Gamma_f. \tag{2.12}$$

The perturbation Γ can be quite general for the purposes of this section; no assumptions about localization of Γ or about random distribution of defects need be made.

B. Optical Theorem

Equation (2.8) can be solved formally for Γ

$$-(\Delta M)M^{-1}z+\Gamma_f=T(z)[I-G(z)T(z)]^{-1}. \tag{2.13}$$

We now write the transpose of this equation for argument z' and make use of the fact that Γ_f, T, and G are symmetric and that ΔM and M are diagonal to obtain

$$\Gamma_f-(\Delta M)M^{-1}z'=[I-T(z')G(z')]^{-1}T(z'). \tag{2.14}$$

We subtract Eq. (2.14) from Eq. (2.13) to obtain

$$\Delta MM^{-1}(z'-z)=T(I-GT)^{-1}-(I-T'G')^{-1}T', \tag{2.15}$$

where we have abbreviated $T\equiv T(z)$, $T'\equiv T(z')$, etc. Multiplying Eq. (2.15) on the left by $(I-T'G')$ and on the right by $(I-GT)$ gives

$$(I-T'G')\Delta MM^{-1}(z'-z)(I-GT)=T-T'-T'(G'-G)T. \tag{2.16}$$

The first important result is obtained by setting $z=\omega^2+i\epsilon$ and $z'=z^*$. Then as $\epsilon\to 0$ we get the *optical theorem*

$$\mathrm{Im}T(\omega^2+i\epsilon)=-T(\omega^2-i\epsilon)\,\mathrm{Im}G(\omega^2+i\epsilon)T(\omega^2+i\epsilon). \tag{2.17}$$

This is a matrix equation. It has been derived by Lippman and Schwinger for quantum-mechanical scattering.[15]

C. Orthonormality

We now verify the orthonormality condition Eq. (2.3) for two expressions of the form of Eq. (2.6). We start with

$$\hat{v}(k'\lambda')^\dagger(I+M^{-1}\Delta M)\hat{v}(k\lambda)=v(k'\lambda')^\dagger(I-T'G')(1+M^{-1}\Delta M)\times(I-GT)v(k\lambda). \tag{2.18}$$

In Eq. (2.18) and in what follows we must set $z=\omega_{k\lambda}{}^2+i\epsilon$ and $z'=\omega_{k'\lambda'}{}^2-i\epsilon$. By adding $(I-T'G')(I-GT)$ to both

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sides of Eq. (2.16), we obtain

$$(I-T'G)(I+M^{-1}\Delta M)(I-GT) = (z'-z)^{-1}[T-T'-T'(G'-G)T] + I-T'G'-GT+T'G'GT. \quad (2.19)$$

The right-hand side of this equation can be simplified by use of the identity

$$G(z')-G(z)=(z'-z)G(z')G(z), \quad (2.20)$$

which follows by direct manipulation of Eq. (2.7). Using Eq. (2.20) one obtains

$$T'G'GT=(z'-z)^{-1}T'(G'-G)T, \quad (2.21)$$

which makes the right side of (2.19) equal to

$$(z'-z)^{-1}(T-T')+I-T'G'-GT.$$

Our trial expression (2.18) now becomes

$$\hat{v}(k'\lambda')^\dagger(I+M^{-1}\Delta M)\hat{v}(k\lambda)=\delta_{kk'}\delta_{\lambda\lambda'}+v(k'\lambda')^\dagger \times[(z'-z)^{-1}(T-T')-T'G'-GT]v(k\lambda). \quad (2.22)$$

From Eq. (2.7) one sees that G' is diagonalized by $v(k\lambda)$:

$$G'v(k\lambda)\equiv G(\omega_{k'\lambda'}{}^2-i\epsilon)v(k\lambda)=(\omega_{k\lambda}{}^2-\omega_{k'\lambda'}{}^2+i\epsilon)^{-1}v(k\lambda)$$

and, similarly,

$$v(k'\lambda')^\dagger G\equiv v(k'\lambda')^\dagger G(\omega_{k\lambda}{}^2+i\epsilon) = v(k'\lambda')^\dagger(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2-i\epsilon)^{-1}.$$

Equation (2.22) then becomes

$$\hat{v}(k'\lambda')^\dagger(I+M^{-1}\Delta M)v(k\lambda)-\delta_{kk'}\delta_{\lambda\lambda'} = (\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2-2i\epsilon)^{-1}[v(k'\lambda')^\dagger Tv(k\lambda) - v(k'\lambda')^\dagger T'v(k\lambda)]-(\omega_{k\lambda}{}^2-\omega_{k'\lambda'}{}^2+i\epsilon)^{-1} \times v(k'\lambda')^\dagger T'v(k\lambda)-(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2-i\epsilon)^{-1} \times v(k'\lambda')^\dagger Tv(k\lambda). \quad (2.23)$$

It is clear that if $\omega_{k\lambda}\neq\omega_{k'\lambda'}$ one can set $\epsilon=0$, and the right-hand side of Eq. (2.23) then equals zero. If $\omega_{k\lambda}=\omega_{k'\lambda'}$, the right-hand side is not literally zero, but it is effectively zero for the following reason: Since one never deals with a single state in a large system such as a crystal, we should integrate Eq. (2.23) over a small region in k' space. It is then permissible to write

$$(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2-2i\epsilon)^{-1}=P(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2)^{-1} +\pi i\delta(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2),$$

$$(\omega_{k\lambda}{}^2-\omega_{k'\lambda'}{}^2+i\epsilon)^{-1}=-P(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2)^{-1} -\pi i\delta(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2),$$

$$(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2-i\epsilon)^{-1}=P(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2)^{-1} +\pi i\delta(\omega_{k'\lambda'}{}^2-\omega_{k\lambda}{}^2).$$

With these expression inserted, the right-hand side of Eq. (2.23) vanishes, thus proving the orthonormality condition for the solutions of the perturbed equations

$$\hat{v}(k'\lambda')^\dagger(I+M^{-1}\Delta M)\hat{v}(k\lambda)=\delta_{kk'}\delta_{\lambda\lambda'}. \quad (2.24)$$

III. PROPERTIES OF THE t-MATRIX

A. Representation of the t-Matrix in Terms of the Eigenvectors of $g\gamma$

We consider a single defect and work in the localized space of γ dealing only with those indices for which $\Gamma\neq 0$. Equation (2.8) becomes

$$t=\gamma-tg\gamma=\gamma-\gamma gt. \quad (3.1)$$

The functional dependence on z is implicit in Eq. (3.1). A solution of this equation by matrix inversion is

$$t=\gamma(1+g\gamma)^{-1}. \quad (3.2)$$

We now consider the eigenvectors $v(\beta)$ and eigenvalues $\mu(\beta)$ of the matrix $g\gamma$:

$$g\gamma v(\beta)=\mu(\beta)v(\beta). \quad (3.3)$$

Eigenvectors belonging to different eigenvalues are orthogonal in the sense

$$v(\beta')^\dagger\gamma v(\beta)=0, \quad \text{unless} \quad \mu(\beta)=\mu(\beta'). \quad (3.4)$$

This statement can be proved by multiplying Eq. (3.3) by $v(\beta')^\dagger\gamma$ to obtain

$$v(\beta')^\dagger\gamma g\gamma v(\beta)=\mu(\beta)v(\beta')^\dagger\gamma v(\beta). \quad (3.5)$$

A similar equation with β and β' interchanged is

$$v(\beta)^\dagger\gamma g\gamma v(\beta')=\mu(\beta')v(\beta)^\dagger\gamma v(\beta'). \quad (3.6)$$

Because g and γ are Hermitian, the left-hand side of Eq. (3.6) equals the left-hand side of Eq. (3.5). Because γ is Hermitian, we have

$$v(\beta')^\dagger\gamma v(\beta)=v(\beta)^\dagger\gamma v(\beta'). \quad (3.7)$$

Subtraction of Eq. (3.6) from (3.5) then yields

$$0=[\mu(\beta)-\mu(\beta')]v(\beta')^\dagger\gamma v(\beta),$$

from which Eq. (3.4) immediately follows. The same orthogonality condition can be assumed to hold for eigenvectors having the same degenerate eigenvalue $\mu(\beta)$, so that we can write

$$v(\beta')^\dagger\gamma v(\beta)=0, \quad \text{unless} \quad \beta=\beta'. \quad (3.4a)$$

The eigenvectors $v(\beta)$ diagonalize t, for we have

$$tv(\beta)=\gamma(1+g\gamma)^{-1}v(\beta)=\gamma v(\beta)[1+\mu(\beta)]^{-1}. \quad (3.8)$$

We then multiply by $v(\beta')^\dagger$ and use Eq. (3.4a) to obtain

$$v(\beta')^\dagger tv(\beta)=v(\beta')^\dagger\gamma v(\beta)[1+\mu(\beta)]^{-1}\delta_{\beta\beta'}. \quad (3.9)$$

We then obtain an explicit representation of the t matrix in terms of the $v(\beta)$ and $\mu(\beta)$:

$$t=\sum_\beta \frac{\gamma v(\beta)v(\beta)^\dagger\gamma}{[1+\mu(\beta)][v(\beta)^\dagger\gamma v(\beta)]}. \quad (3.10)$$

This representation is independent of the normalization of $v(\beta)$. It is a corrected version of Eq. (33) of I.

B. Symmetry Considerations

The matrix g will have the full symmetry of the perfect host crystal, including the point symmetry of the site to be occupied by the defect. The perturbation matrix will have a point symmetry that may be lower than that of g; we call its symmetry group the symmetry group of the defect.

The eigenvectors $v(\beta)$ form bases for irreducible representations of this group. The vectors $gv(\beta)$ and $\gamma v(\beta)$ will be linear combinations of vectors in the same irreducible representation as $v(\beta)$. Two important cases must now be distinguished. *Case (1)*: If this representation occurs only once, then $v(\beta)$ diagonalizes both g and γ [with eigenvalues denoted by $g(\beta)$ and $\gamma(\beta)$], since no other vector can be mixed in. In this case, $v(\beta)$ can be determined by symmetry arguments alone. It will be independent of the strength of γ and of $z=\omega^2+i\epsilon$. The contribution of this βth term to the t-matrix expansion of Eq. (3.10) will then be

$$t_\beta=\gamma(\beta)v(\beta)v(\beta)^\dagger/[1+\mu(\beta)], \tag{3.11}$$

if we assume that $v(\beta)$ is normalized to unity. The eigenvalue of the matrix t_β is

$$t(\beta)=\gamma(\beta)[1+\mu(\beta)]^{-1}. \tag{3.12}$$

Case (2): When more than one representation of the same symmetry is present, we have a small manifold of vectors having the same symmetry that will be mixed by application of g and γ to any one of them. One must then solve the eigenvalue problem of Eq. (3.3) within this manifold. The mixing done by $g\gamma$ will be a function of z and hence of frequency and will also be dependent on the strength of γ. An alternative solution is provided by direct matrix inversion of the equivalent of Eq. (3.2) with g and γ defined only within the manifold.

C. An Example

To illustrate the above discussion and to prepare for actual numerical calculations, we consider the example of a monovalent substitutional impurity in a diatomic crystal having the rocksalt structure. This is a slightly more complicated example than that treated in I. The impurity has a change in mass ΔM and a change in central force constant Δf to its 6 ⟨100⟩ nearest neighbors. The symmetry of the defect is octahedral. The dynamical coordinates of Eq. (2.2) can be expanded in the space of γ in terms of the following symmetry-adapted coordinates that form bases for the irreducible representations of the octahedral group.

An even-parity "breathing" motion of the nearest neighbors having A_{1g} symmetry is

$$q(A_{1g})\equiv 6^{-1/2}[v^{1+}(a\mathbf{1})-v^{1+}(-a\mathbf{1})+v^{2+}(a\mathbf{2})-v^{2+}(-a\mathbf{2}) +v^{3+}(a\mathbf{3})-v^{3+}(-a\mathbf{3})]. \tag{3.13}$$

Two degenerate even-parity "tetragonal" motions of the nearest neighbors having E_g symmetry are

$$q_1(E_g)\equiv 12^{-1/2}[2v^{1+}(a\mathbf{1})-2v^{1+}(-a\mathbf{1})-v^{2+}(a\mathbf{2}) +v^{2+}(-a\mathbf{2})-v^{3+}(a\mathbf{3})+v^{3+}(-a\mathbf{3})], \tag{3.14}$$

$$q_2(E_g)\equiv \tfrac{1}{2}[v^{2+}(a\mathbf{2})-v^{2+}(-a\mathbf{2}) -v^{3+}(a\mathbf{3})+v^{3+}(-a\mathbf{3})]. \tag{3.14'}$$

Three degenerate odd-parity motions of the nearest neighbors having F_{1u} symmetry are

$$q_2(j)\equiv 2^{-1/2}[v^{j+}(a\mathbf{j})+v^{j+}(-a\mathbf{j})], \quad \mathbf{j}=\mathbf{1},\mathbf{2},\mathbf{3}, \tag{3.15}$$

and three degenerate odd-parity motions of the impurity itself having F_{1u} symmetry are

$$q_1(j)\equiv v^{j-}(0), \quad j=1,2,3. \tag{3.16}$$

In Eqs. (3.13)–(3.16) we have used this notation $v^{j\alpha}(L)$, where $j=1, 2, 3$ is a Cartesian component, $\alpha=(+)$ or $(-)$ refers to the type of atom (the impurity is arbitrarily assumed to be located at a negative site at the origin), $\pm a\mathbf{j}$ or 0 is the location of the atom in question, a is the nearest-neighbor distance, and the $\mathbf{j}(j=1, 2, 3)$ are unit vectors along the cube axes. The coefficients of the v's in the above equations form the normalized vectors to be operated upon by g and γ. They will be denoted by $v(A_{1g})$, $v_1(E_g)$, etc.

The two sets of F_{1u} modes will be mixed by g and γ so that, for example, $g\gamma v_2(1)$ is a linear combination of $v_1(1)$ and $v_2(1)$.

The mass-change perturbation matrix Γ_m of Eq. (2.10) couples only to the $v_1(i)$. It is diagonal in each with eigenvalue $-\omega^2\Delta m/m_-$ where m_- is the unperturbed mass of the negative ion.

The change in potential energy can be written in terms of the true atomic displacements $u^{i\alpha}(L)$ as

$$\Delta V=\tfrac{1}{2}\sum_{i=1}^{3}\Delta f\{[u^{i+}(a\mathbf{i})-u^{i-}(0)]^2 +[u^{i+}(-a\mathbf{i})-u^{i-}(0)]^2\}. \tag{3.17}$$

The u's are then converted to the v's by Eq. (2.2), and the v's expressed in terms of the q's of Eqs. (3.13)–(3.16). The result is inserted in Eq. (3.17) to yield

$$\Delta V=\tfrac{1}{2}\Delta f(m_+)^{-1}[q(A_{1g})^2+q_1(E_g)^2+q_2(E_g)^2] +\tfrac{1}{2}\Delta f\sum_{j=1}^{3}[(m_+^{-1})q_2(i)^2+2(m_-)^{-1}q_1(i)^2 -2\sqrt{2}(m_+m_-)^{-1/2}q_1(i)q_2(i)]. \tag{3.18}$$

The matrix γ_f is obtained from the coefficients of the q's in this equation. It is diagonal in $v(A_{1g})$, $v_1(E_g)$, and $v_2(E_g)$, with eigenvalue in each case of $\Delta f/m_+$. The matrix γ_f mixes $v_1(i)$ and $v_2(i)$ so that in this 1-2 manifold we have

$$v_1(i)^\dagger\gamma v_1(i)=v_1(i)^\dagger\gamma_f v_1(i)+v_1(i)^\dagger\gamma_m v_1(i) =2\Delta f/m_- -\omega^2\Delta m/m_-, \tag{3.19}$$

$$v_2(i)^\dagger\gamma v_2(i)=v_2(i)^\dagger\gamma_f v_1(i)=\Delta f/m_+, \tag{3.19'}$$

$$v_2(i)^\dagger\gamma v_1(i)=v_1(i)^\dagger\gamma v_2(i)=v_1(i)^\dagger\gamma_f v_2(i) =-\sqrt{2}\Delta f(m_+m_-)^{-1/2}. \tag{3.19''}$$

The Green's function matrix $G(z)$ can be written as

$$G(z)=\sum_{k\lambda} v(k\lambda)v(k\lambda)^{\dagger}(\omega_{k\lambda}{}^2-z)^{-1}. \quad (3.20)$$

The matrix elements of $G(z)$ [or $g(z)$, since we are now in the space of γ] in the basis defined by Eqs. (3.13)–(3.16) involve the following inner products:

$$v(k\lambda)^{\dagger}v(A_{1g})=(6N)^{-1/2}2i\sum_j \sin k_j a\epsilon_{k\lambda}{}^{j+}, \quad (3.21)$$

$$v(k\lambda)^{\dagger}v_2(E_g)=N^{-1/2}i[\sin k_2 a\epsilon_{k\lambda}{}^{2+}-\sin k_3 a\epsilon_{k\lambda}{}^{3+}], \quad (3.22)$$

$$v(k\lambda)^{\dagger}v_1(j)=N^{-1/2}\epsilon_{k\lambda}{}^{j-}, \quad (3.23)$$

$$v(k\lambda)^{\dagger}v_2(j)=N^{-1/2}\sqrt{2}\epsilon_{k\lambda}{}^{j+}\cos k_j a. \quad (3.24)$$

Here we have used Eq. (2.4) for $v(k\lambda)$. The matrix elements of $g(z)$ that we construct from Eqs. (3.21)–(3.24) reveal that g is diagonalized by $v(A_{1g})$, $v_1(E_g)$, and $v_2(E_g)$ with eigenvalues

$$g(A_{1g})=2(3N)^{-1}\sum_{k\lambda}[\textstyle\sum_j \sin k_j a\epsilon_{k\lambda}{}^{j+}]^2(\omega_{k\lambda}{}^2-z)^{-1} \quad (3.25)$$

and

$$g_1(E_g)=g_2(E_g)=N^{-1}\sum_{k\lambda}[\sin k_2 a\epsilon_{k\lambda}{}^{2+} -\sin k_3 a\epsilon_{k\lambda}{}^{3+}]^2(\omega_{k\lambda}{}^2-z)^{-1}. \quad (3.26)$$

For the odd-parity modes we have

$$v_s(j)^{\dagger}v_{s'}(j')=0, \text{ for } j\neq j' \text{ and } s,s'=1,2; \quad (3.27)$$

$$v_1(j)^{\dagger}v_1(j)=N^{-1}\sum_{k\lambda}[\epsilon_{k\lambda}{}^{j-}]^2(\omega_{k\lambda}{}^2-z)^{-1}; \quad (3.28)$$

$$v_1(j)^{\dagger}gv_2(j)=v_2(j)^{\dagger}gv_1(j)=N^{-1}\sqrt{2}\sum_{k\lambda}\epsilon_{k\lambda}{}^{j-}\epsilon_{k\lambda}{}^{j+} \times\cos k_j a(\omega_{k\lambda}{}^2-z)^{-1}; \quad (3.29)$$

and

$$v_2(j)^{\dagger}gv_2(j)=2N^{-1}\sum_{k\lambda}(\epsilon_{k\lambda}{}^{j+})^2\cos^2 k_j a(\omega_{k\lambda}{}^2-z)^{-1}. \quad (3.30)$$

One then combines these matrix elements for γ and g via the equation

$$v_s(j)^{\dagger}g\gamma v_{s'}(j)=\textstyle\sum_{s''}[v_s(j)^{\dagger}gv_{s''}(j)] \times[v_{s''}(j)^{\dagger}\gamma v_{s'}(j)]. \quad (3.31)$$

The eigenvalues μ of $g\gamma$ for the even modes are

$$\mu(A_{1g})=\Delta f g(A_{1g})/m_+ \quad (3.32)$$

and

$$\mu_1(E_g)=\mu_2(E_g)=\Delta f g_1(E_g)/m_+. \quad (3.33)$$

The eigenvalues for the odd modes result from the diagonalization of the 2×2 matrix $v_s(j)^{\dagger}g\gamma v_{s'}(j)$ of Eq. (3.31). The t matrix then takes the explicit form

$$t=\frac{(\Delta f/m_+)v(A_{1g})v(A_{1g})^{\dagger}}{1+\Delta f g(A_{1g})/m_+}+\frac{\Delta f/m_+}{1+\Delta f g_1(E_g)/m_+} \times[v_1(E_g)v_1(E_g)^{\dagger}+v_2(E_g)v_2(E_g)^{\dagger}] +\sum_{s=1}^{2}\sum_{s'=1}^{2}\sum_{j=1}^{3}v_s(j)v_{s'}(j)^{\dagger} \times[v_s(j)^{\dagger}\gamma(1+g\gamma)^{-1}v_{s'}(j)]. \quad (3.34)$$

In the last term of this equation we have chosen direct matrix inversion instead of the use of eigenvectors in the 1-2 manifold.

IV. PHONON SCATTERING

A. Relaxation Time

We assume a random distribution of scattering centers. The scattering from each center may be very strong, but we assume the concentration of defects to be low enough so that the average scattering throughout the crystal is small. This is the strong-coupling–low-concentration limit. There is another limit worth considering, namely, the weak-coupling–high-concentration limit. An example of this will be discussed in Sec. IVD.

The rate of change of the phonon occupation number N_k for state k (k denotes $\mathbf{k}$ plus λ) is given by the "golden rule":

$$\partial N_k/\partial t=\hbar^{-2}2\pi\textstyle\sum_{k'}\langle|M_{k'\to k}|^2-|M_{k\to k'}|^2\rangle \times\delta(\omega_{k'}-\omega_k). \quad (4.1)$$

The average denoted by $\langle\cdots\rangle$ is over the positions of the defects. In the strong-coupling case, the matrix elements are given by[16]

$$M_{k\to k'}=\tfrac{1}{2}\hbar v(k)^{\dagger}T_{\rm tot}(\omega_k{}^2+i\epsilon)v(k')(N_{k'}+1)^{1/2} \times N_k{}^{1/2}(\omega_k\omega_{k'})^{-1/2}, \quad (4.2)$$

$$M_{k'\to k}=\tfrac{1}{2}\hbar v(k')^{\dagger}T_{\rm tot}(\omega_k{}^2+i\epsilon)v(k)N_{k'}{}^{1/2} \times(N_k+1)^{1/2}(\omega_k\omega_{k'})^{-1/2}. \quad (4.3)$$

Here $T_{\rm tot}$ is the T matrix for the entire crystal obeying the equation

$$T_{\rm tot}=\Gamma_{\rm tot}+\Gamma_{\rm tot}GT_{\rm tot}, \quad (4.4)$$

where $\Gamma_{\rm tot}$ is the total perturbation to the dynamical matrix. This latter quantity will be given by a sum

$$\Gamma_{\rm tot}=\textstyle\sum_L \gamma_L f(L), \quad (4.5)$$

where $f(L)$ is a random variable that takes the value unity with probability c (the fractional defect concentration) and the value zero with probability $1-c$; γ_L represents the contribution of a single defect at site L. Written out in components, γ_L bears this relationship to $\gamma=\gamma_0$ for the same defect at the origin:

$$\gamma_L{}^{j\alpha,j'\alpha'}(\mathbf{L}',\mathbf{L}'')=\gamma^{j\alpha,j'\alpha'}(\mathbf{L}'-\mathbf{L},\mathbf{L}''-\mathbf{L}). \quad (4.6)$$

Luttinger and Kohn have shown that for a resulting scattering probability linear in c, one can write

$$T_{\rm tot}=\textstyle\sum_L t_L f(L), \quad (4.7)$$

where t_L represents the t matrix for the scattering from a single defect at L.[17] It is related to $t(=t_0)$ by an equation exactly like Eq. (4.6),

$$t_L{}^{j\alpha,j'\alpha'}(\mathbf{L}',\mathbf{L}'')=t^{j\alpha,j'\alpha'}(\mathbf{L}'-\mathbf{L},\mathbf{L}''-\mathbf{L}), \quad (4.8)$$

[16] Justification of the use of $T_{\rm tot}$ instead of $\Gamma_{\rm tot}$ in Eqs. (4.2) and (4.3) can be made along the lines used to derive Eq. (1.72) of Ref. 15. See also Refs. 9 and 17.

[17] J. M. Luttinger and W. Kohn, Phys. Rev. **109**, 1892 (1958).

and it obeys the equation

$$t_L=\gamma_L+\gamma_L g t_L. \tag{4.9}$$

When we insert Eqs. (4.2), (4.3), (4.7), and (4.8) into Eq. (4.1), we find that one of the terms to be averaged becomes

$$\langle|M_{k'\to k}|^2\rangle=[\hbar^2(N_{k'}+1)N_k/(4\omega_k\omega_{k'})]|v(k)^\dagger t v(k')|^2 \times\sum_{LL'} e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{L}-\mathbf{L}')}\langle f(\mathbf{L})f(\mathbf{L}')\rangle. \tag{4.10}$$

To lowest order in c, one obtains

$$\langle f(L)f(L')\rangle=c\delta_{LL'},$$

and hence

$$\sum_{LL'} e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{L}-\mathbf{L}')}\langle f(\mathbf{L})f(\mathbf{L}')\rangle=cN, \tag{4.11}$$

where N is the number of unit cells in the crystal. Thus Eq. (4.10) becomes

$$\langle|M_{k'\to k}|^2\rangle=cN\hbar^2(N_{k'}+1)N_k/(4\omega_k\omega_{k'}) \times|v(k)^\dagger t(\omega_k^2+i\epsilon)v(k')|^2, \tag{4.12}$$

just cN times the contribution from a single defect at the origin. A similar result holds for $\langle|M_{k\to k'}|^2\rangle$.

Equation (4.1) then becomes

$$\partial N_k/\partial t=\tfrac{1}{2}\pi cN\sum_{k'}|v(k)^\dagger t(\omega_k^2+i\epsilon)v(k')|^2 \times(\omega_k\omega_{k'})^{-1}\delta(\omega_k-\omega_{k'})(N_{k'}-N_k). \tag{4.13}$$

To obtain a phonon lifetime we set $N_{k'}=0$ for $k\neq k'$ and define

$$-\partial N_k/\partial t\equiv N_k/\tau_k. \tag{4.13'}$$

We use the relation [derivable from Eqs. (2.7) and (3.20)]

$$(2\omega_k)^{-1}\delta(\omega_k-\omega_{k'})=\delta(\omega_k^2-\omega_{k'}^2)=\pi^{-1}\,\mathrm{Im}(\omega_{k'}^2-\omega_k^2-i\epsilon) =\pi^{-1}\,\mathrm{Im}v(k')^\dagger G(\omega_k^2+i\epsilon)v(k'), \tag{4.14}$$

and the completeness of the $v(k')$ to derive the result

$$\omega_k\tau_k^{-1}=cN\sum_{k'}\mathrm{Im}[v(k)^\dagger t(\omega_k^2-i\epsilon)v(k')] \times[v(k')^\dagger G(\omega_k^2+i\epsilon)v(k')][v(k')^\dagger t(\omega_k^2+i\epsilon)v(k)] =cN\,\mathrm{Im}[v(k)^\dagger t(\omega_k^2+i\epsilon)G(\omega_k^2+i\epsilon)t(\omega_k^2+i\epsilon)v(k)]. \tag{4.15}$$

The optical theorem (2.17) allows us to write this as

$$\omega_k\tau_k^{-1}=-cN\,\mathrm{Im}[v(k)^\dagger t(\omega_k^2+i\epsilon)v(k)]. \tag{4.16}$$

This expression is independent of N because of the normalization of the $v(k)$'s given by Eq. (2.4). A further rewriting follows by use of Eq. (3.10):

$$\omega_k\tau_k^{-1} =cN\sum_\beta\frac{[v(k)^\dagger\gamma v(\beta)][v(\beta)^\dagger\gamma v(k)]\,\mathrm{Im}\mu(\beta)}{\{[1+\mathrm{Re}\mu(\beta)]^2+[\mathrm{Im}\mu(\beta)]^2\}[v(\beta)^\dagger\gamma v(\beta)]}. \tag{4.17}$$

Thus the "modes" β contribute additively to τ_k^{-1}. A sophisticated derivation of Eq. (4.16) has been given by Maradudin[8] for the MDA where $\gamma_f=0$.

For our example of the substitutional impurity we can use Eq. (3.34) to obtain

$$\tau_k^{-1}=[\tau_k(A_{1g})]^{-1}+[\tau_k(E_g)]^{-1}+[\tau_k(\mathrm{odd})]^{-1}, \tag{4.18}$$

where

$$\omega_k[\tau_k(A_{1g})]^{-1}=\frac{cN|v(k)^\dagger v(A_{1g})|^2(\Delta f/m_+)^2\,\mathrm{Img}(A_{1g})}{[1+\Delta f\,\mathrm{Reg}(A_{1g})/m_+]^2+[\Delta f\,\mathrm{Img}(A_{1g})/m_+]^2}, \tag{4.19}$$

$$\omega_k[\tau_k(E_g)]^{-1}=\frac{cN[|v(k)^\dagger v_1(E_g)|^2+|v(k)^\dagger v_2(E_g)|^2](\Delta f/m_+)^2\,\mathrm{Img}_1(E_g)}{[1+\Delta f\,\mathrm{Reg}_1(E_g)/m_+]^2+[\Delta f\,\mathrm{Img}_1(E_g/m_+]^2}, \tag{4.20}$$

and

$$\omega_k[\tau_k(\mathrm{odd})]^{-1}=-cN\sum_{\substack{s,s';\\ s'',j}}[v(k)^\dagger v_s(j)][v_{s'}(j)^\dagger v(k)][v_s(j)^\dagger\gamma v_{s''}(j)]\,\mathrm{Im}[v_{s''}(j)^\dagger(1+g\gamma)^{-1}v_{s'}(j)]. \tag{4.21}$$

All matrix elements of g in Eqs. (4.19)–(4.21) are to be evaluated for $z=\omega_k^2+i\epsilon$ as $\epsilon\to 0^+$.

B. Implications for Lattice Thermal Conductivity

The quantity τ_k can be characterized as the lifetime of a phonon as limited by impurity scattering. For thermal conductivity calculations this is not necessarily the relaxation time to use, even if three-phonon processes and other processes can be neglected. In such calculations[12] one sets the right-hand side of Eq. (4.13) with $N_k=N_k^0+n_k$ ($N_k^0=\langle N_k\rangle_{\text{thermal}}$; $n_k=$ first-order deviation) equal to

$$(\partial N_k/\partial t)_{\text{drift}}=\mathbf{v}_\mathbf{k}\cdot\nabla T dN_k^0/dT, \tag{4.22}$$

where $\mathbf{v}_{k\lambda}=\partial\omega_{k\lambda}/\partial\mathbf{k}$ is the phonon group velocity. The result is a Boltzmann equation:

$$\mathbf{v}_\mathbf{k}\cdot\nabla T dN_k^0/dT=cN\pi(2\omega_k^2)^{-1}\sum_{k'}|v(k)^\dagger t(\omega_k+i\epsilon)v(k)|^2 \times\delta(\omega_{k'}-\omega_k)(n_{k'}-n_k). \tag{4.23}$$

It is well known that the only solutions of Eq. (4.23) that are required are those of odd parity in k. The term with $n_{k'}$ in this equation is necessary only if $|v(k)^\dagger t v(k')|^2$ has an important part that is odd in k'. If the defect site has inversion symmetry, we can break the sum over β in Eq. (3.10) into even (g) and odd (u) parts, $t=t_g+t_u$, so that $v(k)^\dagger t_g v(k')$ is even in k and k', and $v(k)^\dagger t_u v(k')$

is odd in k and k'. Equation (4.23) then becomes

$$\mathbf{v}_k\cdot\nabla T dN_k^0/dT = -n_k\tau_k^{-1}+cN\pi(2\omega_k^2)^{-1}\sum_{k'}\{[v(k)^\dagger t_g(\omega_k^2-i\epsilon)v(k')] \times[v(k')^\dagger t_u(\omega_k^2+i\epsilon)v(k)]+[v(k)^\dagger t_u(\omega_k^2-i\epsilon)v(k')] \times[v(k')^\dagger t_g(\omega_k^2+i\epsilon)v(k)]\}\delta(\omega_{k'}-\omega_k)n_{k'}. \quad (4.24)$$

If either t_u or t_g dominates t, the second or cross term in Eq. (4.24) will be negligible compared with $-n_k\tau_k^{-1}$, and τ_k will be a thermal conductivity relaxation time as well as a lifetime. In this case, scattering from $\mathbf{k}$ to $\mathbf{k}'$ is just as likely as scattering from $\mathbf{k}$ to $-\mathbf{k}'$, and memory of direction is lost after one collision.

If t_g and t_u are comparable in magnitude, the second term in Eq. (4.24) will be important. For numerical work it is perhaps best to solve this equation by iteration starting with the equation (∇T along z axis):

$$n_k=-\tau_k(dT/dz)(dN_k^0/dT)v_{kz}-cN\tau_k\pi(2\omega_k^2)^{-1} \times\sum_{k'}K(k,k')n_{k'}\delta(\omega_{k'}-\omega_k), \quad (4.25)$$

where $K(k,k')$ stands for the expression in curly brackets in Eq. (4.24). Such a procedure has been proposed by Carruthers.[12]

C. Long-Wavelength, Weak-Coupling Limit

This limit for acoustical phonons should lead to Rayleigh scattering where

$$\tau_k^{-1}\sim\omega_k^4. \quad (4.26)$$

"Weak coupling" means we set the denominators equal to unity in Eqs. (4.19) and (4.20) and set

$$[-\mathrm{Im}(1+g\gamma)^{-1}]\approx\mathrm{Im}g\gamma$$

in Eq. (4.21). We also make use of Eq. (4.14) and note that for small ω

$$\sum_{k\lambda}\delta(\omega_{k\lambda}^2-\omega^2)=\sum_{k'\lambda'}\pi\delta(\omega_{k'\lambda'}-\omega)/2\omega\sim\omega.$$

Thus for small ω we have from Eqs. (3.25) and (3.26),

$$g_1(A_{1g})\sim\omega^3,\quad g_1(E_g)\sim\omega^3,\quad g_2(E_g)\sim\omega^3, \quad (4.27)$$

and

We also have from Eqs. (3.21) and (3.22) that $v(k)^\dagger v(A_{1g})$ and $v(k)^\dagger v_{1,2}(E_g)\sim\omega$. These frequency dependences when inserted in Eqs. (4.19) and (4.20) yield the Rayleigh limit of Eq. (4.26) for $\tau_k(A_{1g})$ and $\tau_k(E_g)$.

The odd modes are more difficult to treat in this limit. The 1-2 basis of Eqs. (3.15) and (3.16) is not suitable for estimates of this kind. Another basis, the 1′-2′ basis, is more suitable. In the new basis the vectors $v_2'(j)$ are equivalent to the vectors $|0_i\rangle$ of I, and the matrix γ_f couples only to them. The transformation equations to the primed basis are

$$v_2'(j)=(m_-+2m_+)^{-1/2}[-(2m_+)^{1/2}v_1(j)+(m_-)^{1/2}v_2(j)], \quad (4.28)$$

$$v_1'(j)=(m_-+2m_+)^{-1/2}[(m_-)^{1/2}v_1(j)+(2m_+)^{1/2}v_2(j)]. \quad (4.28a)$$

The coefficients in these equations define an orthogonal matrix S.

In the new coordinate system the matrices γ' and g' are given by equations of the type $\gamma'=S\gamma S^{-1}$. Thus in the 1′-2′ system we can derive these results,

$$\gamma_f'=\begin{pmatrix}0 & 0\\ 0 & 2\Delta f/m_-+\Delta f/m_+\end{pmatrix}, \quad (4.29)$$

$$\gamma_m'=\frac{-\Delta m\omega^2/m_-}{m_-+2m_+}\begin{pmatrix}m_- & -(2m_-m_+)^{1/2}\\ -(2m_-m_+)^{1/2} & 2m_+\end{pmatrix}, \quad (4.30)$$

from Eqs. (3.19), (3.19a), and (3.19b). The inner products that are needed to calculate g' are determined directly from Eqs. (4.28), (4.28a), (3.21), (3.22), (3.23), and (3.24):

$$v(k\lambda)^\dagger v_1'(j)=N^{-1/2}(m_-+2m_+)^{-1/2}[(m_-)^{1/2}\epsilon_{k\lambda}{}^{j-}+2(m_+)^{1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a], \quad (4.31)$$

$$v(k\lambda)^\dagger v_2'(j)=(m_-+2m_+)^{-1/2}N^{-1/2}(2m_+m_-)^{1/2}\times[-(m_-)^{-1/2}\epsilon_{k\lambda}{}^{j-}+(m_+)^{-1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a]. \quad (4.32)$$

Note the limiting behavior of Eqs. (4.31) and (4.32) for small k acoustical phonons

$$v(k\lambda)^\dagger v_1'(j)\to\text{const}, \quad (4.33)$$

$$v(k\lambda)^\dagger v_2'(j)\sim k^2. \quad (4.34)$$

The last relation follows from the fact that the relative physical displacements of the positive and negative ions must tend to zero like k^2 as k tends to zero which means that

$$(m_+)^{-1/2}\epsilon_{k\lambda}{}^{+}-(m_-)^{-1/2}\epsilon_{k\lambda}{}^{-}\sim k^2. \quad (4.35)$$

The matrix elements of g in the new basis can now be calculated from Eqs. (4.31) and (4.32)

$$v_1'(j)^\dagger g v_1'(j)=N^{-1}(m_-+2m_+)^{-1}\sum_{k\lambda}[(m_-)^{1/2}\epsilon_{k\lambda}{}^{j-}+2(m_+)^{1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a]^2(\omega_{k\lambda}^2-z)^{-1}, \quad (4.36)$$

$$v_2'(j)^\dagger g v_2'(j)=N^{-1}(m_-+2m_+)^{-1}(2m_+m_-)\sum_{k\lambda}[-(m_-)^{-1/2}\epsilon_{k\lambda}{}^{j-}+(m_+)^{-1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a]^2(\omega_{k\lambda}^2-z)^{-1}, \quad (4.37)$$

$$v_1'(j)^\dagger g v_2'(j)=v_2'(j)^\dagger g v_1'(j)=N^{-1}(m_-+2m_+)(2m_+m_-)^{1/2}\sum_{k\lambda}[(m_-)^{-1/2}\epsilon_{k\lambda}{}^{j-}+2(m_+)^{1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a]\times[-(m_-)^{-1/2}\epsilon_{k\lambda}{}^{j-}+(m_+)^{-1/2}\epsilon_{k\lambda}{}^{j+}\cos k_j a](\omega_{k\lambda}^2-z)^{-1}. \quad (4.38)$$

The weak-coupling limit of Eq. (4.21) in the 1′-2′ basis is

$$\omega_k[\tau_k(\text{odd})]^{-1}=cN\sum_{s,s'\atop s'',s''',j}[v(k)^\dagger v_s'(j)][v_{s'}'(j)^\dagger v(k)][v_s'(j)^\dagger\gamma v_{s''}'(j)]\,\mathrm{Im}\{[v_{s''}'(j)^\dagger g v_{s'''}'(j)][v_{s'''}'(j)^\dagger\gamma v_{s'}'(j)]\}. \quad (4.39)$$

From this equation one can conclude, with the help of Eqs. (4.29)–(4.38), that in the small k limit for acoustical phonons $[\tau_k(\text{odd})]^{-1}$ indeed goes like $\omega_k{}^4$.

The quadratic behavior of $v(k\lambda)^\dagger v_2'(j)$ in Eq. (4.34) is not shared by $v(k\lambda)^\dagger v_2(j)$, which tends to a constant as does $v(k\lambda)^\dagger v_1(j)$. When the proper combination of $v_1(j)$ and $v_2(j)$ is taken to form $v_2'(j)$ in Eq. (4.28), cancellation of the constant limits occurs, leaving the second-order limit. In actual calculations using the 1-2 basis this cancellation will have to occur in numerically computed quantities, and the numbers may not be precise enough for this to happen. With the 1′-2′ basis, on the other hand, the proper small k behavior is guaranteed by the functional form of the expressions fed as input to the computer.

D. Isotope Scattering in a Diatomic Crystal

The naturally occurring isotopes will furnish additional scattering of phonons beyond that taken into account in the t matrix of Eq. (4.23). Isotopes occur in high concentrations, but the over-all scattering is weak; they thus provide an example of the "weak-coupling–high-concentration" limit mentioned in Sec. IVA. In this limit it is appropriate to calculate the scattering to first order in $\langle(\delta m/m)^2\rangle$.

A pure mass change will involve a perturbation γ that couples only to odd-parity configurations of the type in Eq. (3.16). The g-u cross term of Eq. (4.24) is therefore missing, and the phonon lifetime τ_k is the thermal conductivity relaxation time. The derivation of the expression for τ_k in this case parallels that of Sec. IVA. We start with Eq. (4.1) but use Γ_{tot} instead of T_{tot} in Eqs. (4.2) and (4.3), where now we have $\Gamma_{\text{tot}}=\Gamma_{\text{is}}$ and

$$\Gamma_{\text{is}}{}^{jj'\alpha\alpha'}(\mathbf{L},\mathbf{L}')=-(m_\alpha)^{-1}\delta m_\alpha(\mathbf{L})\delta_{\alpha\alpha'}\delta_{LL'}\delta_{jj'}\omega^2, \quad (4.40)$$

where $\delta m_\alpha(\mathbf{L})$ is a random variable representing the deviation of the mass of the αth atom at site $\mathbf{L}$ from the average mass m_α. We postpone the averaging, but otherwise follow the earlier derivation to obtain the result [similar to Eq. (4.15)]

$$\omega_k[\tau_k(\text{is})]^{-1}=\text{Im}[v(k)^\dagger\langle\Gamma_{\text{is}}G(\omega_k{}^2+i\epsilon)\Gamma_{\text{is}}\rangle v(k)]. \quad (4.41)$$

The matrix product appearing in this equation can be written explicitly as

$$\begin{aligned}&\text{Im}\langle\Gamma_{\text{is}}G\Gamma_{\text{is}}\rangle^{jj',\alpha\alpha'}(L,L')\\&\quad=\text{Im}\Big\langle\sum_{j''j'''}\sum_{\alpha''\alpha'''}\sum_{L''L'''}(m_\alpha)^{-1}\omega_k{}^4\delta m_\alpha(L)\\&\quad\times\delta_{\alpha\alpha''}\delta_{LL''}\delta_{jj''}G^{j''j''',\alpha''\alpha'''}(L'',L''')(m_{\alpha'''})^{-1}\\&\qquad\times\delta m_{\alpha'''}(L''')\delta_{\alpha'''\alpha'}\delta_{L'''L'}\delta_{j'''j'}\Big\rangle. \quad (4.42)\end{aligned}$$

The average can be performed before the summations to give to lowest order in $\langle(\delta m/m)^2\rangle$

$$\begin{aligned}&\langle(m_\alpha)^{-1}\delta m_\alpha(L)(m_{\alpha'''})^{-1}\delta m_{\alpha'''}(L''')\rangle\\&\qquad=\langle(\delta m_\alpha/m_\alpha)^2\rangle\delta_{\alpha\alpha'''}\delta_{LL'''}. \quad (4.43)\end{aligned}$$

Equation (4.42) then becomes

$$\begin{aligned}&\text{Im}\langle\Gamma_{\text{is}}G\Gamma_{\text{is}}\rangle^{jj',\alpha\alpha'}(L,L')\\&\quad=\text{Im}\omega_k{}^4\langle(\delta m_\alpha/m_\alpha)^2\rangle G^{jj',\alpha\alpha}(L,L)\delta_{LL'}\delta_{\alpha\alpha'}\\&\quad=\pi\omega_{k\lambda}{}^4\langle(\delta m_\alpha/m_\alpha)^2\rangle\sum_{k'\lambda'}N^{-1}\epsilon_{k'\lambda'}{}^{j\alpha}\epsilon_{k'\lambda'}{}^{j'\alpha}\\&\qquad\times\delta(\omega_{k'\lambda'}{}^2-\omega_{k\lambda})\delta_{LL'}. \quad (4.44)\end{aligned}$$

We have used Eqs. (3.20) and (2.4) to write the elements of ImG.

The relaxation time is then given by inserting this result in Eq. (4.41) and using Eqs. (2.4) and (4.14)

$$\begin{aligned}&[\tau_{k\lambda}(\text{is})]^{-1}\\&\quad=\pi(2N)^{-1}\omega_{k\lambda}{}^2\sum_{k'\lambda'}[\langle(\delta m_+/m_+)^2\rangle|\,\boldsymbol{\varepsilon}_{k\lambda}{}^+\cdot\boldsymbol{\varepsilon}_{k'\lambda'}{}^+|^2\\&\qquad+\langle(\delta m_-/m_-)^2\rangle|\,\boldsymbol{\varepsilon}_{k\lambda}{}^-\cdot\boldsymbol{\varepsilon}_{k'\lambda'}{}^-|^2]\delta(\omega_{k'\lambda'}-\omega_{k\lambda}). \quad (4.45)\end{aligned}$$

Because of the relation (4.35) the term in square brackets in this equation has this small k acoustical limit

$$\begin{aligned}&(m_+)^{-2}|\,\boldsymbol{\varepsilon}_{k\lambda}{}^+\cdot\boldsymbol{\varepsilon}_{k'\lambda'}{}^+|^2\langle(\delta m_++\delta m_-)^2\rangle\\&\qquad=(m_+)^{-2}|\,\boldsymbol{\varepsilon}_{k\lambda}{}^+\cdot\boldsymbol{\varepsilon}_{k'\lambda'}{}^+|^2\langle[\delta(m_++m_-)]^2\rangle. \quad (4.46)\end{aligned}$$

One should also note the ω^4 Rayleigh dependence that follows from

$$\sum_{k'\lambda'}\delta(\omega_{k'\lambda'}-\omega_{k\lambda})\sim\omega_{k\lambda}{}^2.$$

Equation (4.45) represents the generalization of Eqs. (5.13) and (5.14) of Carruthers's article.[12] Because isotopes and any strongly coupled impurities will not be correlated, the respective scattering from the two types of defect will not interfere, and one should add the scattering rates or reciprocals of the relaxation times in the Boltzmann equation.

V. CONCLUDING REMARK

If one is to use realistic expressions like Eqs. (4.18) through (4.21), Eq. (4.25), and Eq. (4.45) to describe the contribution of defects to the scattering term in the Boltzmann equation for the thermal conductivity, one has to come to grips in a fairly realistic way with the role of three-phonon processes in modifying the resulting expressions for n_k. This has not yet been accomplished.

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