

Thermal conductivity for phonon scattering by substitutional defects in crystals

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The thermal conductivity of a harmonic Bravais crystal containing randomly distributed substitutional defects due to impurity-phonon scattering is theoretically investigated using the methods of double-time thermal Green's functions and Kubo formalism considering nondiagonal terms in the heat-current operator as proposed by Hardy. Mass changes as well as force-constant changes between impurity atom and host-lattice atoms are taken into account explicitly. It is shown that the total conductivity can be written as a sum of two contributions, namely, diagonal and nondiagonal contributions. For phonons of small half-width, the former has precisely the same form which is obtained from Boltzmann's transport equation for impurity scattering in the relaxation-time approximation. An analytical expression for the inverse relaxation time due to impurity scattering is obtained in the low-concentration limit of randomly distributed impurities and it shows non-Rayleigh behavior. The non-Rayleigh terms are held responsible for the asymmetric depression in the peak of the thermal-conductivity curves observed experimentally in doped crystals. It is found that the mass change and force-constant change make reinforcing or cancelling contributions to the inverse relaxation time according to whether they are of equal or of opposite signs.

I. INTRODUCTION

Experimental investigations¹ of the temperature dependence of the thermal conductivity of alkali-halide crystals doped with various defects have led to several interesting results. Firstly, the thermal conductivity is diminished due to the scattering of phonons by defect atoms; the depressions in the thermal-conductivity curves being asymmetric with respect to the peak, implying a non-Rayleigh scattering of phonons in the system. In many cases pronounced "dips," usually on the low-temperature side of the maximum of the thermal-conductivity curve, are found and these have been ascribed² to the resonance scattering of phonons from quasi-localized modes of the impure crystal associated with heavy impurities. Certain experiments³ show virtually no Rayleigh scattering at low temperatures, contrary to the Klemens⁴ theory which tacitly assumes that mass-defect scattering and force-constant change scattering reinforce each other. Krumhansl and Matthew⁵ have shown that in the case of a linear chain of atoms for low-frequency phonons, mass and force-constant change scatterings may compensate each other so that the combined scattering linewidth due to both processes is less than if only one scattering mechanism was present.

In recent years, many theoretical studies have been devoted to the lattice thermal conductivity of crystals containing point defects using various models and approximations. In general, two basic approaches have been followed. The first of these, which is most frequently used, is based on the Boltzmann transport equation for phonons scattered by impurities in the relaxation-time approximation.⁶⁻⁸ Although plausible, this approach suffers

from the usual shortcomings of the kinetic theories as has been again enumerated by Hardy.⁹ The second approach is based on the results from the general theory of irreversible processes in which thermal conductivity is related to the correlation functions of the heat currents.^{10,11} Such an approach is more rigorous and provides a systematic method to include the low-frequency phonons and interference between the various scattering mechanisms. The crux of the problem lies in the determination of the functional dependence of the heat-current operator on the dynamical variables of the system. Within the last few years much theoretical work has been done on the behavior of the thermal conductivity of lattices with substitutional impurities using correlation-function formalism and various models and approximations.¹²⁻¹⁶ Attempts¹⁷⁻²² have also been made to explain the "dips" in the thermal-conductivity curves in terms of resonance scattering processes, but at low temperatures, when only long-wavelength phonons are present, all these theories reduce to the Rayleigh law for the scattering of phonons.

Most of the work on the scattering of phonons by point defects has been confined to the model of isotopic impurity or the so-called mass-defect approximation in which the difference between the mass of the impurity and that of the atom it replaces characterizes the perturbation. The change in force constants between the impurity and its neighbors has not been considered. This seems somewhat unreasonable since in actual practice the introduction of defects also modifies the force constants between the impurity atom and the host atoms. It would be of interest to investigate the thermal conductivity of a crystal with substitutional defects taking into account both mass and force-

constant changes. Some results²³⁻²⁶ have recently been obtained for the scattering of phonons from a defect considering a change of mass and a change of simple force constant to the nearest neighbors in the relaxation-time approximation. We rely here on the Kubo formalism²⁷ which is more rigorous and permits calculations of finer details.

In the present paper we have evaluated an expression for the thermal conductivity of a harmonic Bravais crystal for the scattering of lattice waves by randomly distributed substitutional impurities considering nondiagonal terms in the heat-current operator.²⁸ The principle advanced is the use of the Kubo correlation-function expression for the thermal conductivity and the method of double-time thermal Green's functions.²⁹ Simultaneous changes in mass and force constants due to the introduction of impurities in the host crystal are taken into account. The effects of force-constant changes are treated in the low-concentration limit. It is shown that the total conductivity can be separated into two contributions, namely, diagonal and nondiagonal contributions. The former in the limiting case reduces to the expression derived from the Boltzmann transport equation applied to the phonon gas. An analytical expression for the inverse relaxation time due to the impurity scattering is obtained for low concentration of randomly distributed impurities in the Debye model. Thereby experimental results mentioned earlier are explained.

II. THEORY

The starting point for our calculation of the lattice thermal conductivity is the Kubo expression given by^{10,11}

$$K = \lim_{\epsilon \rightarrow 0} \frac{k_B \beta}{3V} \int_0^\infty dt e^{-\epsilon t} \int_0^\beta d\lambda \langle \vec{Q}(0) \cdot \vec{Q}(t + i\hbar\lambda) \rangle. \quad (1)$$

Here k_B is the Boltzmann constant, V is the volume of the crystal, \hbar is Planck's constant divided by 2π , $\beta = (k_B T)^{-1}$, T being the absolute temperature, $\vec{Q}(t)$ is the heat-current operator of the lattice in the Heisenberg representation, and the angular brackets indicate the thermal average over the canonical ensemble described by the Hamiltonian.

As is evident from (1), the evaluation of thermal conductivity with the aid of Kubo formula requires a knowledge of the heat current operator. Maradudin¹² and Hardy²⁸ have derived a general expression for the heat-current operator for a three-dimensional crystal with imperfections and anharmonic forces and have shown that even in the harmonic approximation the total heat-current operator contains a term which is nondiagonal in the phonon branch indices in addition to the usual diagonal term. The total heat current operator as derived by Hardy²⁸ can be written

$$\vec{Q}(t) = \vec{Q}_{0d}(t) + \vec{Q}_{0nd}(t), \quad (2)$$

where $\vec{Q}_{0d}(t)$ and $\vec{Q}_{0nd}(t)$ represent the diagonal and nondiagonal parts of the heat-current operator, respectively. The diagonal contribution $\vec{Q}_{0d}(t)$ is given by

$$\vec{Q}_{0d}(t) = \sum_{\vec{k}j} \hbar \omega_{\vec{k}j} \vec{v}_{\vec{k}j} N_{\vec{k}j}(t), \quad (3)$$

where $\vec{v}_{\vec{k}j} = \partial \omega_{\vec{k}j} / \partial \vec{k}$ and $\omega_{\vec{k}j}$ are the group velocity and frequency of the normal mode with wave vector \vec{k} and polarization index j , and $N_{\vec{k}j}(t) = a_{\vec{k}j}^\dagger(t) a_{\vec{k}j}(t)$ is the number-density operator, $a_{\vec{k}j}^\dagger(t)$ and $a_{\vec{k}j}(t)$ being the phonon creation and annihilation operators in the Heisenberg representation. The nondiagonal part $\vec{Q}_{0nd}(t)$ contains contributions from modes of same wave vector but different polarization directions and in terms of phonon operators $A_{\vec{k}j}$ and $B_{\vec{k}j}$, it can be written

$$\vec{Q}_{0nd}(t) = \frac{1}{2} \sum_{\vec{k}j, j'}' \hbar \omega_{\vec{k}j} \vec{v}_{\vec{k}j, j'} A_{\vec{k}j}(t) B_{\vec{k}j'}^\dagger(t), \quad (4)$$

where $\vec{v}_{\vec{k}j, j'}$ ($j \neq j'$) is a generalized velocity given by

$$v_{\vec{k}j, j'} = \frac{\omega_{\vec{k}j}^2 - \omega_{\vec{k}j'}^2}{2\omega_{\vec{k}j}} \sum_\alpha e_\alpha(\vec{k}j) \frac{\partial e_\alpha(\vec{k}j')}{\partial \vec{k}}. \quad (5)$$

The prime over the summation shows that $j \neq j'$ and the phonon operators $A_{\vec{k}j}$ and $B_{\vec{k}j}$ are defined by

$$A_{\vec{k}j} = a_{\vec{k}j} + a_{-\vec{k}j}^\dagger = A_{-\vec{k}j}^\dagger,$$

$$B_{\vec{k}j} = a_{\vec{k}j} - a_{-\vec{k}j}^\dagger = -B_{-\vec{k}j}^\dagger.$$

The contribution $\vec{Q}_{0d}(t)$ is the expression which is commonly used for the phonon heat current operator in a crystal.

Substituting the expression (2) for $\vec{Q}(t)$ into Eq. (1) and decoupling the two-particle correlation functions into one-particle correlation functions, and noting that only correlation functions with different time arguments contribute to conductivity, the expression for the thermal conductivity can be written

$$K = K_0 + K_1, \quad (6)$$

with

$$K_0 = \frac{\hbar^2 k_B \beta}{3V} \sum_{\vec{k}j} \sum_{\vec{k}'j'}' \vec{v}_{\vec{k}j} \cdot \vec{v}_{\vec{k}'j'} \omega_{\vec{k}j} \omega_{\vec{k}'j'} \times \int_0^\infty dt e^{-\epsilon t} \int_0^\beta d\lambda F_{\vec{k}j, \vec{k}'j'}(t + i\hbar\lambda), \quad (7)$$

and

$$K_1 = \frac{\hbar^2 k_B \beta}{12V} \sum_{\vec{k}j, j'}' \sum_{\vec{k}_1 j_1 j_1'}' \vec{v}_{\vec{k}j, j'} \cdot \vec{v}_{\vec{k}_1 j_1 j_1'} \omega_{\vec{k}j} \omega_{\vec{k}_1 j_1} \times \int_0^\infty dt e^{-\epsilon t} \int_0^\beta d\lambda F_{\vec{k}j, \vec{k}_1 j_1 j_1'}(t + i\hbar\lambda), \quad (8)$$

where limit $\epsilon \rightarrow 0$ is implied. The correlation functions F are given by

$$F_{\vec{k}, \vec{k}', j'}(t) = \langle a_{\vec{k}, j}^\dagger(0) a_{\vec{k}', j'}(t) \rangle \langle a_{\vec{k}, j}(0) a_{\vec{k}', j'}^\dagger(t) \rangle \quad (9)$$

and

$$F_{\vec{k}, j', \vec{k}_1, j_1}(t) = \langle A_{\vec{k}, j}(0) B_{\vec{k}_1, j_1}^\dagger(t) \rangle \langle B_{\vec{k}, j}^\dagger(0) A_{\vec{k}_1, j_1}(t) \rangle \\ + \langle A_{\vec{k}, j}(0) A_{\vec{k}_1, j_1}(t) \rangle \langle B_{\vec{k}, j}^\dagger(0) B_{\vec{k}_1, j_1}^\dagger(t) \rangle. \quad (10)$$

In Eq. (9) we have ignored terms involving two creation and two annihilation operators because they do not correspond to physical processes in normal matter. The first term in Eq. (6) describes the contribution of the diagonal part of the heat-current operator to the thermal conductivity and the second term gives the nondiagonal contribution.

The correlation functions occurring in Eqs. (9) and (10) can be evaluated by several methods.³⁰ Here we evaluate them by means of the double-time Green's-function technique as discussed by Zu-

barev²⁹ on a harmonic model of the crystal.

III. HAMILTONIAN AND GREEN'S FUNCTIONS

We consider a three-dimensional Bravais crystal with volume V containing N atoms such that p lattice sites are occupied by substitutional impurities each of mass M' , while the remaining $N-p$ lattice sites are occupied by identical host atoms of mass M . The introduction of impurity leads to simultaneous changes in mass and the force constants between the host atoms and an impurity atoms. If it is assumed that the impurities are distributed randomly and their concentration (p/N) is quite small, then one can assume that the distance between any two impurities is so large that the impurity-impurity interaction can be neglected. The changes in the force constant between impurity and host atoms may be assumed to be significant only to nearest neighbors. The total Hamiltonian of such a defect crystal in the harmonic approximation can be written

$$H = \sum_{n\alpha} \frac{p_\alpha^2(n)}{2M} + \frac{1}{2} \sum_{n\alpha} \sum_{n'\beta} \Phi_{\alpha\beta}(n, n') u_\alpha(n) u_\beta(n') + \sum_{i\alpha} \left(\frac{1}{2M'} - \frac{1}{2M} \right) p_\alpha^2(i) + \frac{1}{2} \sum_{n\alpha} \sum_{n'\beta} \Delta\Phi_{\alpha\beta}(n, n') u_\alpha(n) u_\beta(n'). \quad (11)$$

In this expression the symbol n denotes the position of an atomic site and i designates the position of the impurity; $u_\alpha(n)$ and $p_\alpha(n)$ are the α Cartesian components of the displacement and momentum vectors of the n th atom, M and M' are the masses of normal and impurity atoms; $\Phi_{\alpha\beta}(n, n')$ are the harmonic force constants for the crystal; and $\Delta\Phi_{\alpha\beta}(n, n') [= \Phi'_{\alpha\beta}(n, n') - \Phi_{\alpha\beta}(n, n')]$ represents the change in the force constant due to the introduction of the defect atoms. The primed Φ 's represent the

force constants that have been changed due to the impurities. The summation over n and n' in the last term is nonvanishing only if either n or n' correspond to the site of an impurity.

We now define the weighted harmonic mean M_0 of the masses of all the atoms in the defect crystal by the relation

$$1/M_0 = f/M' + (1-f)/M,$$

with $f = p/N$. Equation (11) can now be rewritten

$$H = \sum_{n\alpha} \frac{p_\alpha^2(n)}{2M_0} + \frac{1}{2} \sum_{n\alpha} \sum_{n'\beta} \Phi_{\alpha\beta}(n, n') u_\alpha(n) u_\beta(n') + \frac{f}{2\mu} \sum_{n\alpha} p_\alpha^2(n) - \frac{1}{2\mu} \sum_{i\alpha} p_\alpha^2(i) + \frac{1}{2} \sum_{n\alpha} \sum_{n'\beta} \Delta\Phi_{\alpha\beta}(n, n') u_\alpha(n) u_\beta(n'), \quad (12)$$

where $\mu = MM'/(M' - M)$. We now express the components $u_\alpha(n)$ and $p_\alpha(n)$ in terms of phonon operators as³⁰

$$u_\alpha(n) = \left(\frac{\hbar}{2M_0 N} \right)^{1/2} \sum_k \frac{e_\alpha(k)}{(\omega_k)^{1/2}} e^{i\vec{k} \cdot \vec{R}(n)} A_k, \quad (13)$$

$$p_\alpha(n) = -i \left(\frac{\hbar M_0}{2N} \right)^{1/2} \sum_k e_\alpha(k) (\omega_k)^{1/2} e^{i\vec{k} \cdot \vec{R}(n)} B_k,$$

where $\vec{R}(n)$ labels the equilibrium position vector of the n th atom in the crystal, ω_k is the angular frequency of the normal mode of a system in which each lattice site is occupied by an atom of mass M_0 , and $\vec{e}(k)$ is the polarization vector. One might call M_0 the effective atomic mass as seen by the

phonons in the crystal. The Hamiltonian of the crystal in second-quantized notation can be expressed as

$$H = H_0 + H', \quad (14)$$

where

$$H_0 = \sum_k \hbar \omega_k (a_k^\dagger a_k + \frac{1}{2}) \quad (14a)$$

and

$$H' = -\hbar \sum_{k_1, k_2} C(k_1, k_2) B_{k_1} B_{k_2} \\ + \hbar \sum_{k_1, k_2} D(k_1, k_2) A_{k_1} A_{k_2}. \quad (14b)$$

The first term (H_0) is the Hamiltonian of a perfect lattice and is the exactly solvable part. The second term (H') is the perturbation part of the Hamiltonian which gives rise to scattering of phonons. For the sake of convenience, here and in what follows, we use one index k as short for pair of indices $\vec{k}j$. The expressions for $C(k_1, k_2)$ and $D(k_1, k_2)$ are given by

$$C(k_1, k_2) = \frac{1}{\mu} \frac{M_0}{4N} (\omega_{k_1} \omega_{k_2})^{1/2} \vec{\epsilon}(k_1) \cdot \vec{\epsilon}(k_2) \times \left(\sum_n^N f e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{R}(n)} - \sum_i^p e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{R}(i)} \right) \quad (15a)$$

and

$$D(k_1, k_2) = \frac{1}{4NM_0} (\omega_{k_1} \omega_{k_2})^{-1/2} \sum_{\alpha\beta} \sum_{n'n''} \Delta\Phi_{\alpha\beta}(n, n') \times e_{\alpha}(k_1) e_{\beta}(k_2) e^{i[\vec{k}_1 \cdot \vec{R}(n) + \vec{k}_2 \cdot \vec{R}(n')]}. \quad (15b)$$

$C(k_1, k_2)$ vanishes when p is either 0 or N . Using the relation

$$\Delta\Phi(n, n') = -\sum_{n''} \Delta\Phi(n, n''),$$

where the prime on the summation denotes that $n' \neq n$, $D(k_1, k_2)$ can be rewritten

$$D(k_1, k_2) = \frac{1}{4NM_0} (\omega_{k_1} \omega_{k_2})^{-1/2} \sum_{\alpha\beta} e_{\alpha}(k_1) e_{\beta}(k_2) \times \sum_{n, n'} \Delta\Phi_{\alpha\beta}(n, n') e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{R}(n)} \times (e^{i\vec{k}_2 \cdot [\vec{R}(n) - \vec{R}(n')]}) - 1), \quad (16)$$

where, as mentioned earlier, the lattice sites n

and n' refer to the impurity and its nearest-neighbor host atoms.

To evaluate the correlation functions appearing in Eqs. (9) and (10) we introduce the following one-particle retarded Green's functions:

$$G_{kk'}^{(1)}(t-t') = \langle\langle a_k(t); a_{k'}^{\dagger}(t') \rangle\rangle, \quad (17a)$$

$$G_{kk'}^{(2)}(t-t') = \langle\langle A_k(t); B_{k'}^{\dagger}(t') \rangle\rangle, \quad (17b)$$

$$G_{kk'}^{(3)}(t-t') = \langle\langle A_k(t); A_{k'}(t') \rangle\rangle, \quad (17c)$$

$$G_{kk'}^{(4)}(t-t') = \langle\langle B_k^{\dagger}(t); B_{k'}^{\dagger}(t') \rangle\rangle. \quad (17d)$$

The Fourier transform of the equation of motion of the Green's function (17a) is

$$\bar{n}\omega G_{kk'}^{(1)}(\omega) = (\bar{n}/2\pi) \langle\langle a_k(t), a_{k'}^{\dagger}(t') \rangle\rangle_{t=t'} + \langle\langle [a_k(t), H]; a_{k'}^{\dagger}(t') \rangle\rangle_{\omega}, \quad (18)$$

which, for Hamiltonian (14), becomes

$$(\omega - \omega_k) G_{kk'}^{(1)}(\omega) = \delta_{kk'} / 2\pi + \lambda_{kk'}(\omega), \quad (19)$$

where $\lambda_{kk'}(\omega)$ is the Fourier transform of the Green's function

$$\lambda_{kk'}(t-t') = \langle\langle M_k(t); a_{k'}^{\dagger}(t') \rangle\rangle, \quad (20)$$

with

$$M_k(t) = 2 \sum_{k_1} [C(-k, k_1) B_{k_1}(t) + D(-k, k_1) A_{k_1}(t)]. \quad (21)$$

Considering the equation of motion for the Green's function $\lambda_{kk'}(t-t')$ with respect to time argument t' and Fourier transforming the result, we obtain

$$(\omega - \omega_k) \lambda_{kk'}(\omega) = (1/\pi) [C(-k, k') + D(-k, k')] + f_{kk'}(\omega)/\pi, \quad (22)$$

where

$$f_{kk'}(\omega) = 4\pi \sum_{k_1, k_2} [D(-k, k_1) D(k', k_2) L_{k_1 k_2}^{(1)}(\omega) - D(-k, k_1) C(k', k_2) L_{k_1 k_2}^{(2)}(\omega) + C(-k, k_1) D(k', k_2) L_{k_1 k_2}^{(3)}(\omega) - C(-k, k_1) C(k', k_2) L_{k_1 k_2}^{(4)}(\omega)], \quad (23)$$

in which we introduced the following one-phonon Green's functions:

$$L_{k_1 k_2}^{(1)}(\omega) = \langle\langle A_{k_1}(t); A_{k_2}(t') \rangle\rangle_{\omega}, \quad (24a)$$

$$L_{k_1 k_2}^{(2)}(\omega) = \langle\langle A_{k_1}(t); B_{k_2}(t') \rangle\rangle_{\omega}, \quad (24b)$$

$$L_{k_1 k_2}^{(3)}(\omega) = \langle\langle B_{k_1}(t); A_{k_2}(t') \rangle\rangle_{\omega}, \quad (24c)$$

$$L_{k_1 k_2}^{(4)}(\omega) = \langle\langle B_{k_1}(t); B_{k_2}(t') \rangle\rangle_{\omega}. \quad (24d)$$

If we use Eq. (22) in Eq. (19), the Green's function $G_{kk'}^{(1)}(\omega)$ can be written in the form of Dyson equation

$$G_{kk'}^{(1)}(\omega) = G_k^0(\omega) \delta_{kk'} + G_k^0(\omega) \bar{P}_{kk'}^{(1)}(\omega) G_{kk'}^{(1)}(\omega) = G_k^0(\omega) \delta_{kk'} + G_k^0(\omega) \Pi_{kk'}^{(1)}(\omega) G_{kk'}^{(1)}(\omega), \quad (25)$$

where

$$G_k^0(\omega) = 1/2\pi(\omega - \omega_k) \quad (26)$$

and

$$\bar{P}_{kk'}^{(1)}(\omega) = 4\pi [C(-k, k') + D(-k, k')] + 4\pi f_{kk'}(\omega). \quad (27)$$

The Dyson equation can be rewritten to give the diagonal component of the Green's function as

$$G_{kk}^{(1)}(\omega) = \delta_{kk}^0 / [(G_k^0)^{-1} - \Pi_k^{(1)}(\omega)], \quad (28)$$

where the diagonal polarization operator $\Pi_k^{(1)}(\omega)$ is given by

$$\Pi_k^{(1)}(\omega) = \frac{\bar{P}_k^{(1)}(\omega) G_k^0(\omega)}{G_{kk}^{(1)}(\omega)} = \bar{P}_k^{(1)}(\omega) [1 + G_k^0(\omega) \bar{P}_k^{(1)}(\omega)]^{-1}. \quad (29)$$

In the range of frequencies ω far from the zeros of the denominator in Eq. (29), one may expand the right-hand side in a power series of $\tilde{P}_k(\omega)$. In the first approximation retaining only the first term, i. e., $\Pi_k^{(1)}(\omega) \simeq \tilde{P}_k^{(1)}(\omega)$, Eq. (28) gives

$$G_{kk'}^{(1)}(\omega) = \frac{\delta_{kk'}}{2\pi[\omega - \tilde{\omega}_k^{(1)} - P_k^{(1)}(\omega)]}, \quad (30)$$

where $\tilde{\omega}_k^{(1)}$ is the renormalized frequency of the mode $\tilde{k}j$ in the lowest approximation of the perturbation theory and is given by

$$\tilde{\omega}_k^{(1)} = \omega_k + 2[C(-k, k) + D(-k, k)] \quad (31)$$

and

$$P_k^{(1)}(\omega) = 2f_k(\omega). \quad (32)$$

The Green's function (30) can be evaluated in successive approximations as discussed in an earlier paper.³¹ For the sake of simplicity, it is evaluated here in the first approximation of the self-energy function $P_k^{(1)}(\omega)$. In this approximation, the Green's functions $L(\omega)$ appearing in Eqs. (24) are obtained by means of the corresponding zeroth-order Green's function

$$(G_{kk'}^{(1)}(\omega))^0 = \delta_{kk'}/2\pi(\omega - \tilde{\omega}_k^{(1)}). \quad (33)$$

The self-energy function is obtained in this way up to second order in the defect parameters C and D . The frequency spectrum of the Green's function (33) can be described by the zeroth-order renormalized Hamiltonian

$$H_{\text{ren}}^0 = \frac{\hbar}{4} \sum_k \tilde{\omega}_k^{(1)} (A_k^\dagger A_k + B_k^\dagger B_k). \quad (34)$$

Writing the equations of motion of the Green's functions (24) with the help of Eq. (34), we obtain

$$L_{kk'}^{(1)}(\omega) = \tilde{\omega}_k^{(1)} \delta_{k, -k'} / \pi [\omega^2 - (\tilde{\omega}_k^{(1)})^2], \quad (35a)$$

$$L_{kk'}^{(2)}(\omega) = -\omega \delta_{k, -k'} / \pi [\omega^2 - (\tilde{\omega}_k^{(1)})^2], \quad (35b)$$

$$L_{kk'}^{(3)}(\omega) = \omega \delta_{k, -k'} / \pi [\omega^2 - (\tilde{\omega}_k^{(1)})^2], \quad (35c)$$

$$L_{kk'}^{(4)}(\omega) = -\tilde{\omega}_k^{(1)} \delta_{k, -k'} / \pi [\omega^2 - (\tilde{\omega}_k^{(1)})^2]. \quad (35d)$$

Using Eqs. (35) in Eq. (23), we obtain from Eq. (32)

$$\begin{aligned} P_k^{(1)}(\omega) = & 8 \sum_{k_1} [\omega^2 - (\tilde{\omega}_k^{(1)})^2]^{-1} \{ \tilde{\omega}_k^{(1)} [C^2(-k, k_1) \\ & + D^2(-k, k_1)] + \omega [C(-k, k_1)D^*(-k, k_1) \\ & + C^*(-k, k_1)D(-k, k_1)] \}. \end{aligned} \quad (36)$$

For a small quantity ϵ tending to zero, we can write

$$P_k^{(1)}(\omega + i\epsilon) = \Delta_k^{(1)}(\omega) - i\Gamma_k^{(1)}(\omega),$$

where the real part $\Delta_k^{(1)}(\omega)$ represents the shift in frequency of the k th mode in the j th branch of the spectrum, while the imaginary part $\Gamma_k^{(1)}(\omega)$ gives the half-width of the phonons of wave vector k . From Eq. (36), the explicit expressions for them are given by

$$\begin{aligned} \Delta_k^{(1)}(\omega) = & 8\mathcal{O} \sum_{k_1} [\omega^2 - (\tilde{\omega}_k^{(1)})^2]^{-1} \{ \tilde{\omega}_k^{(1)} [C^2(-k, k_1) \\ & + D^2(-k, k_1)] + \omega [C(-k, k_1)D^*(-k, k_1) \\ & + C^*(-k, k_1)D(-k, k_1)] \} \end{aligned} \quad (37)$$

and

$$\begin{aligned} \Gamma_k^{(1)}(\omega) = & 4\pi \sum_{k_1} \{ [C^2(-k, k_1) + D^2(-k, k_1)] \\ & \times [\delta(\omega - \tilde{\omega}_k^{(1)}) - \delta(\omega + \tilde{\omega}_k^{(1)})] \\ & + [C(-k, k_1)D^*(-k, k_1) + C^*(-k, k_1) \\ & \times D(-k, k_1)] [\delta(\omega - \tilde{\omega}_{k_1}^{(1)}) + \delta(\omega + \tilde{\omega}_{k_1}^{(1)})] \}, \end{aligned} \quad (38)$$

where \mathcal{O} denotes the principal part. With this result, the Green's function (30) can be written

$$G_{kk'}^{(1)}(\omega + i\epsilon) = \frac{\delta_{kk'}}{2\pi[\omega - \epsilon_k^{(1)}(\omega) + i\Gamma_k^{(1)}(\omega)]}, \quad (39a)$$

where

$$\epsilon_k^{(1)}(\omega) = \tilde{\omega}_k^{(1)} + \Delta_k^{(1)}(\omega) \quad (40)$$

and $\tilde{\omega}_k^{(1)}$ is given by Eq. (31).

Proceeding in a similar way with the equations of motion of the Green's functions (17b)–(17d) and following the above procedure, we obtain

$$G^{(2)}(\omega + i\epsilon) = \frac{\omega \delta_{kk'}}{\pi \{ \omega^2 - [\epsilon_k^{(2)}(\omega)]^2 + i 2\omega_k \Gamma_k^{(2)}(\omega) \}}, \quad (39b)$$

$$G^{(3)}(\omega + i\epsilon) = \frac{\omega_k \delta_{k, -k'}}{\pi \{ \omega^2 - [\epsilon_k^{(3)}(\omega)]^2 + i 2\omega_k \Gamma_k^{(3)}(\omega) \}}, \quad (39c)$$

$$G^{(4)}(\omega + i\epsilon) = -\frac{\omega_k \delta_{k, -k'}}{\pi \{ \omega^2 - [\epsilon_k^{(4)}(\omega)]^2 + i 2\omega_k \Gamma_k^{(4)}(\omega) \}}, \quad (39d)$$

where

$$[\epsilon_k^{(i)}(\omega)]^2 = (\tilde{\omega}_k^{(i)})^2 + 2\omega_k \Delta_k^{(i)}(\omega); \quad i = 2, 3, 4, \quad (40a)$$

with

$$(\tilde{\omega}_k^{(2)})^2 = \omega_k^2 + 4\omega_k [C(-k, k) + D(-k, k)], \quad (40b)$$

$$(\tilde{\omega}_k^{(3)})^2 = \omega_k^2 + 4\omega_k [C^*(k, -k) + D^*(k, -k)], \quad (40c)$$

$$(\tilde{\omega}_k^{(4)})^2 = \omega_k^2 + 4\omega_k [C(k, -k) + D(k, -k)]. \quad (40d)$$

Here $\Delta_k^{(i)}(\omega)$ and $\Gamma_k^{(i)}(\omega)$ are the real and imaginary parts of $P_k^{(i)}(\omega)$ given by

$$P_k^{(2)}(\omega) = 8 \sum_{k_1} [\omega^2 - (\tilde{\omega}_{k_1}^{(2)})^2]^{-1} \left(\frac{1}{\omega_{k_1}} [(\tilde{\omega}_{k_1}^{(2)})^2 C^2(k, -k_1) + \omega_{k_1}^2 D^2(k, -k_1)] + \frac{1}{\omega_k} [\omega_k^2 C(k, -k_1) D^*(k, -k_1) + \omega^2 C^*(k, -k_1) D(k, -k_1)] \right), \quad (41a)$$

$$P_k^{(3)}(\omega) = 8 \sum_{k_1} [\omega^2 - (\tilde{\omega}_k^{(3)})^2]^{-1} \left[\frac{1}{\omega_{k_1}} \left(\frac{\omega^2}{\omega_k} (\tilde{\omega}_{k_1}^{(3)})^2 C^2(-k, k_1) + \omega_{k_1}^2 D^2(-k, k_1) \right) + \frac{\omega^2}{\omega_k} [C(-k, k_1) D^*(-k, k_1) + C^*(-k, k_1) D(-k, k_1)] \right], \quad (41b)$$

$$P_k^{(4)}(\omega) = 8 \sum_{k_1} [\omega^2 - (\tilde{\omega}_k^{(4)})^2]^{-1} \left[\frac{1}{\omega_{k_1}} \left((\tilde{\omega}_{k_1}^{(4)})^2 C^2(k, k_1) + \frac{\omega^2}{\omega_k} (\tilde{\omega}_{k_1}^{(4)})^2 D^2(k, k_1) \right) + \frac{\omega^2}{\omega_k} [C(k, k_1) D^*(k, k_1) + C^*(k, k_1) D(k, k_1)] \right]. \quad (41c)$$

Having obtained the Green's function, we can obtain the correlation function from the relation

$$\langle a_{k'}^\dagger(t') a_k(t) \rangle = \int_{-\infty}^{\infty} d\omega J_{kk'}^{(1)}(\omega) e^{-i\omega(t-t')}, \quad (42)$$

where $J_{kk'}^{(1)}(\omega)$ is the spectral density function and is related to the Green's function through the relation

$$J_{kk'}^{(1)}(\omega) = \frac{i}{e^{\beta\hbar\omega} - 1} [G_{kk'}^{(1)}(\omega + i\epsilon) - G_{kk'}^{(1)}(\omega - i\epsilon)]. \quad (43)$$

IV. THERMAL CONDUCTIVITY

We evaluate the diagonal and nondiagonal contributions to the thermal conductivity separately.

Substituting the values of correlation functions appearing in Eq. (9) with the help of Eqs. (17a), (42), and (43), the diagonal part K_0 of the thermal conductivity is given by

$$K_0 = \lim_{\epsilon \rightarrow 0} -\frac{\hbar^2 k_B \beta}{3V} \sum_{k, k'} \omega_k \omega_{k'} \tilde{v}_k \cdot \tilde{v}_{k'} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 n(\omega_1) n(\omega_2) \times \tilde{G}_{kk'}^{(1)}(\omega_1) \tilde{G}_{kk'}^{(1)}(\omega_2) e^{\beta\hbar\omega_2} \int_0^{\infty} dt e^{-t\tau} \int_0^{\beta} d\lambda e^{-i(\omega_1 - \omega_2)t} e^{\lambda\hbar(\omega_1 - \omega_2)}, \quad (44)$$

where for convenience we have written

$$\tilde{G}_{kk'}(\omega) = G_{kk'}(\omega + i\epsilon) - G_{kk'}(\omega - i\epsilon),$$

and $n(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$. Performing the integration over t and λ , K_0 becomes

$$K_0 = \frac{-\hbar^2 k_B \beta^2 \pi}{3V} \sum_{k, k'} \omega_k \omega_{k'} \tilde{v}_k \cdot \tilde{v}_{k'} \times \int_0^{\infty} d\omega n^2(\omega) e^{\beta\hbar\omega} \tilde{G}_{kk'}^{(1)}(\omega) \tilde{G}_{kk'}^{(1)}(\omega). \quad (45)$$

With the help of Eq. (39a) the above equation reduces to

$$K_0 = \frac{\hbar^2 k_B \beta^2}{3\pi V} \sum_k \omega_k^2 v_k^2 \int_{-\infty}^{\infty} d\omega n^2(\omega) \times e^{\beta\hbar\omega} \frac{[\Gamma_k^{(1)}(\omega)]^2}{\{[\omega - \epsilon_k^{(1)}(\omega)]^2 + [\Gamma_k^{(1)}(\omega)]^2\}^2}. \quad (46)$$

For small value of the half-width $\Gamma_k^{(1)}(\omega)$, the integrand in Eq. (46) has a sharp maximum around $\omega \simeq \epsilon_k^{(1)}$ and the integral can be evaluated analytically

by replacing the peak distribution by a Dirac δ function. We then obtain the following expression for the thermal conductivity:

$$K_0 = \frac{\hbar^2 k_B \beta^2}{3V} \sum_k \omega_k^2 v_k^2 \frac{e^{\beta\hbar\epsilon_k^{(1)}}}{(e^{\beta\hbar\epsilon_k^{(1)}} - 1)^2} \frac{1}{\Gamma_k^{(1)}(\epsilon_k^{(1)})}. \quad (47)$$

The inverse relaxation time or the scattering width of phonons is given by

$$\tau_k^{-1} = \Gamma_k(\epsilon_k^{(1)}). \quad (48)$$

Neglecting the shift in the frequency of phonons, Eq. (47) has precisely the same form which can be obtained from Boltzmann transport equation for impurity scattering in the so-called relaxation time approximation and discussed by Klemens⁷ and others.⁸ It is obtained here as a direct consequence of Kubo formula and the choice of the Hamiltonian.

In Eq. (38), only positive values of the frequency are meaningful. The phonon wave vector \tilde{k}_1 can take values only within the first Brillouin zone. Replacing the summation over \tilde{k}_1 by an integration in the usual manner we can write

$$\begin{aligned} \Gamma_k^{(1)}(\epsilon_k^{(1)}) &= \frac{4\pi V}{(2\pi)^3} \int k_1^2 dk_1 \sin\theta d\theta d\phi \\ &\times [C^2(-k, k_1) + D^2(-k, k_1) + C(-k, k_1) \\ &\times D^*(-k, k_1) + C^*(-k, k_1)D(-k, k_1)] \delta(\epsilon_k^{(1)} - \omega_{k_1}^{(1)}), \end{aligned} \quad (49)$$

where (θ, ϕ) denotes the direction of \vec{k}_1 with respect to \vec{k} . Because of the δ function, the integration is to be carried out over modes of constant energy in wave-vector space satisfying the relation

$$\vec{\omega}_{k_1}^{(1)} = \omega_{k_1} + 2D(-k_1, k_1) = \epsilon_k^{(1)}. \quad (50)$$

In the Debye approximation, which is reasonably accurate for low-frequency phonons and hence at low T , $\omega_k = kc$, where c is the phonon group velocity. Considering terms up to second order in perturbation theory, Eq. (49) becomes

$$\begin{aligned} \Gamma_k^{(1)}(\epsilon_k^{(1)}) &= \frac{2V}{\pi c^3} \omega_k^2 \frac{1}{4\pi} \\ &\times \int d\Omega [C^2(-k, k_1) + D^2(-k, k_1) \\ &+ C(-k, k_1)D^*(-k, k_1) \\ &+ C^*(-k, k_1)D(-k, k_1)]_{\vec{k}_1=\vec{k}}. \end{aligned} \quad (51)$$

Setting $C(k, k) = \omega_k C'(k, k)$ and $D(k, k) = \omega_k^{-1} D'(k, k)$, we obtain

$$\begin{aligned} \Gamma_k^{(1)}(\epsilon_k^{(1)}) &= \frac{2V}{\pi c^3} \{ \omega_k^4 C'^2(k, k) + \omega_k^2 [C'(k, k)D'(k, k) \\ &+ C'(k, k)D'^*(k, k) + D'^2(k, k) + D'^2(-k, k)] \}_A, \end{aligned} \quad (52)$$

where the suffix A denotes the directional average of the quantities in the curly brackets. If the force-constant change is ignored, $\Gamma_k^{(1)}$ and hence inverse relaxation time due to pure mass scattering becomes proportional to the fourth power of phonon frequency ω_k and the square of mass change $M' - M$.

Equation (52) gives the inverse relaxation time for the scattering of phonons due to substitutional defects in a Bravais crystal. The first term proportional to the fourth power of the phonon frequency ω_k and square-mass difference $M' - M$ gives the usual Rayleigh scattering law, and is similar to that obtained by the others^{7,8} using the Boltzmann equation. Because of the introduction of force constant change the frequency dependence of the inverse relaxation time is no longer of the form ω_k^4 only, but contains a term proportional to ω_k^2 besides

a frequency-independent term. For this frequency dependence of τ^{-1} the maximum contributions from the ω^0 and ω^2 terms to the depression in the thermal conductivity curve will occur at low temperatures and will decrease with temperature, while the ω^4 term becomes strong in the region above the peak. Hence for temperatures tending to zero, we expect that the curves for different concentration of isotopic impurities in the pure mass defect scattering approximation approach each other tangentially. This agrees with experiments³ on isotopic scattering in alkali halides doped with monovalent impurities. The experiments^{32,33} on the conductivity of alkali halides containing various concentrations of divalent impurities show two striking features. The experimental curves do not approach each other at low temperatures and also while the depression at temperatures above the maximum is appreciable, the low-temperature depression is enormous. This behavior can be qualitatively understood from our expression for τ^{-1} by assuming that the force constant change scattering is such that the contribution from the frequency-independent and ω^2 terms is appreciable and reinforces the ω^4 scattering. Then at low temperatures there will be an additional contribution to ω^4 scattering from the ω^0 and ω^2 terms. This additional contribution will decrease with the rise of temperature where the effects of ω^4 scattering will become more effective. In some cases, the processes due to change in mass and force constants may mutually compensate so that the simultaneous effect of both processes would give a higher value of conductivity than when one scattering mechanism was present. The experimental results for KCl doped with iodine corresponds to this situation.² The non-Rayleigh scattering terms may thus be held responsible for the experimental asymmetry in the peak of the thermal conductivity curves, inexplicable in terms of the Klemens theory.⁴ The magnitude and signs of defect parameters C and D will decide the extent of the asymmetry.

We now consider the nondiagonal part K_1 of the thermal conductivity due to the nondiagonal term in the heat current operator. If we make use of Eqs. (17b), (17c), and (17d), together with (42) and (43) in Eq. (10), we see that K_1 can be written in the form

$$K_1 = K_1' + K_1'', \quad (53)$$

where

$$K_1' = -\frac{\pi \hbar^2 k_B \beta^2}{12V} \sum_{\vec{k}_1, \vec{k}_2} \sum_{\vec{k}_1, \vec{k}_2} \vec{v}_{\vec{k}_1, \vec{k}_2} \cdot \vec{v}_{\vec{k}_1, \vec{k}_2} \omega_{\vec{k}_1} \omega_{\vec{k}_2} \int_{-\infty}^{\infty} d\omega n^2(\omega) e^{\beta \hbar \omega} \tilde{G}_{\vec{k}_1, \vec{k}_2}^{(2)}(\omega) \tilde{G}_{\vec{k}_1, \vec{k}_2}^{(2)}(\omega), \quad (54a)$$

and

$$K_1'' = -\frac{\pi\hbar^2 k_B \beta^2}{12V} \sum'_{\mathbf{k}, j, j'} \sum'_{\mathbf{k}_1, j_1, j_1'} \tilde{v}_{\mathbf{k}, j, j'} \cdot \tilde{v}_{\mathbf{k}_1, j_1, j_1'} \omega_{\mathbf{k}, j} \omega_{\mathbf{k}_1, j_1} \int_{-\infty}^{\infty} d\omega n^2(\omega) e^{\beta\hbar\omega} \bar{G}_{\mathbf{k}_1, j_1, \mathbf{k}, j}^{(3)}(\omega) \bar{G}_{\mathbf{k}, j, \mathbf{k}_1, j_1}^{(4)}(\omega). \quad (54b)$$

With the help of Eq. (39b), Eq. (54a) becomes

$$K_1' = \frac{4\hbar^2 k_B \beta^2}{3V\pi} \sum'_{\mathbf{k}, j, j'} \sum'_{\mathbf{k}_1, j_1, j_1'} \tilde{v}_{\mathbf{k}, j, j'} \cdot \tilde{v}_{\mathbf{k}_1, j_1, j_1'} \omega_{\mathbf{k}, j} \omega_{\mathbf{k}_1, j_1} \\ \times \int_{-\infty}^{\infty} d\omega \frac{n^2(\omega) e^{\beta\hbar\omega} \omega^2 \omega_{\mathbf{k}, j} \omega_{\mathbf{k}_1, j_1} \Gamma_{\mathbf{k}, j}^{(2)}(\omega) \Gamma_{\mathbf{k}_1, j_1}^{(2)}(\omega) \delta_{\mathbf{k}, j} \delta_{\mathbf{k}_1, j_1} \delta_{j, j'}}{(\{\omega^2 - [\epsilon_{\mathbf{k}, j}^{(2)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}, j}^2 [\Gamma_{\mathbf{k}, j}^{(2)}(\omega)]^2)(\{\omega^2 - [\epsilon_{\mathbf{k}_1, j_1}^{(2)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}_1, j_1}^2 [\Gamma_{\mathbf{k}_1, j_1}^{(2)}(\omega)]^2)} \\ = \frac{4\hbar^2 k_B \beta^2}{3V\pi} \sum'_{\mathbf{k}, j, j'} \tilde{v}_{\mathbf{k}, j, j'} \cdot \tilde{v}_{\mathbf{k}, j, j'} \omega_{\mathbf{k}, j}^2 \omega_{\mathbf{k}, j}^2 \int_{-\infty}^{\infty} d\omega \frac{n^2(\omega) e^{\beta\hbar\omega} \omega^2 \Gamma_{\mathbf{k}, j}^{(2)}(\omega) \Gamma_{\mathbf{k}, j}^{(2)}(\omega)}{(\{\omega^2 - [\epsilon_{\mathbf{k}, j}^{(2)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}, j}^2 [\Gamma_{\mathbf{k}, j}^{(2)}(\omega)]^2)(\{\omega^2 - [\epsilon_{\mathbf{k}, j}^{(2)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}, j}^2 [\Gamma_{\mathbf{k}, j}^{(2)}(\omega)]^2)}. \quad (55)$$

Similarly the expression for K_1'' is given by

$$K_1'' = \frac{4\hbar^2 k_B \beta^2}{3V\pi} \sum'_{\mathbf{k}, j, j'} \tilde{v}_{\mathbf{k}, j, j'}^2 \omega_{\mathbf{k}, j}^3 \omega_{\mathbf{k}, j}^3 \int_{-\infty}^{\infty} d\omega \frac{n^2(\omega) e^{\beta\hbar\omega} \Gamma_{\mathbf{k}, j}^{(3)}(\omega) \Gamma_{\mathbf{k}, j}^{(4)}(\omega)}{(\{\omega^2 - [\epsilon_{\mathbf{k}, j}^{(3)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}, j}^2 [\Gamma_{\mathbf{k}, j}^{(3)}(\omega)]^2)(\{\omega^2 - [\epsilon_{\mathbf{k}, j}^{(4)}(\omega)]^2\}^2 + 4\omega_{\mathbf{k}, j}^2 [\Gamma_{\mathbf{k}, j}^{(4)}(\omega)]^2)}. \quad (56)$$

In the approximation which yielded Eq. (47), i. e., replacing of integrand by renormalized δ function, the nondiagonal contributions [Eqs. (55) and (56)] can be written in the form very similar to the diagonal results, involving mixing of the phonons. However, for finite $\Gamma_{\mathbf{k}, j}^{(i)}$, the contribution K_1 is of higher order in the impurity concentration than K_0 .

V. DISCUSSION

Equations (46), (55), and (56) give the expression for the thermal conductivity of a defect Bravais crystal due to phonon scattering by randomly distributed substitutional impurities considering the change in the force constants. For phonons of small half-width, the diagonal contribution reduces to the familiar expression as obtained, for example, by Klemens⁷ from Boltzmann transport equation. Due to the modification of force constants, the frequency dependence of inverse relaxation time and half-width is no longer of the form ω^4 , but contains a frequency-independent term and a term proportional to ω^2 arising from force constant changes. The latter produces asymmetry in the peak of the conductivity term as obtained experimentally.¹ The inverse relaxation time of the pure isotope scattering is approximately proportional to the fourth power of phonon frequency and square of mass change, and is similar to what Klemens⁴ has obtained using the Boltzmann equation and is particularly valid for low-frequency phonons. Equation (52) shows that the mass change and force constant change make reinforcing or cancelling contributions to the inverse relaxation time according to whether they are of equal or of opposite signs, respectively. This result agrees with the one-dimensional calculations of Krumhansl and Matthew⁵ employing Green's-func-

tion technique. Expressions (55) and (56) show that the nondiagonal contribution K_1 due to the nondiagonal part of the heat current operator comes from modes with different state of polarizations. These equations give corrections to the Boltzmann equation for the thermal conductivity. At low temperatures, when only those phonons which suffer negligible impurity scattering are excited, the diagonal contribution is expected to give a reasonable approximation to the conductivity of a crystal with impurities. At higher temperatures, the full form should be used. Hardy,²⁸ using classical treatment for the phonon operators in Eq. (4), has argued that the nondiagonal heat current operator $\bar{Q}_{\text{ond}}(t)$ is made up of an oscillating function of terms whose frequencies are the sum and difference of the frequencies of different branches and as a result it gives negligible contribution to the thermal conductivity in comparison to the diagonal one when averaged over a long period of time. The present study shows that there is a finite contribution of the nondiagonal part of the heat current operators to the thermal conductivity, though expected to be much smaller than the diagonal contribution. The exact magnitude of K_1 is not possible without using some specific model for the crystal.

It emerges from the present study that from the Kubo formalism, using the double-time thermal Green's function technique, the thermal conductivity of a crystal can be obtained with a comparative ease. Further the relaxation time of the phonon scattering by impurities can be estimated with much finer details than from the conventional transport theory. It may be mentioned that the results obtained here are correct to the lowest order in the concentration of the minority species.

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