PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Thermal Conductivity of an Anharmonic Crystal

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(Received 1 September 1971)

An expression is obtained for the lattice thermal conductivity of an anharmonic crystal by the method of double-time Green's functions using the energy-flux operator propounded by Hardy. The study uses cubic and quartic anharmonic terms in the crystal Hamiltonian. It is found that the nondiagonal part of the energy-flux operator gives a finite contribution to the transport of energy, though its contribution is small compared to that from the diagonal part.

I. INTRODUCTION

The general theory of the lattice contribution to the thermal conductivity of a solid, first given by Peierls,[1] is based on the Boltzmann transport equation for phonon scattering in crystals. This approach has been extensively applied and discussed in the literature,[2-4] though the theoretical basis has been changed. Recent theories of phonon transport in solid express the thermal conductivity in terms of the correlation functions of the thermal flux. The crux of the problem lies in the determination of functional dependence of the energy-flux operator on the dynamical variables of the system. The form usually used for the energy flux $\vec{Q}(t)$ in the lattice is the Peierls expression based on the spherically symmetric dispersion formula and is given by

$$\vec{Q}(t)=\sum_{\vec{k}s} \hbar\omega_{\vec{k}s} N_{\vec{k}s}(t)\vec{v}_{\vec{k}s} , \qquad (1)$$

where $\vec{v}_{\vec{k}s}$ is the group velocity of the normal mode with wave vector $\vec{k}$ and polarization index s, $\omega_{\vec{k}s}$ is the frequency of the phonon in the mode $\vec{k}s$, and $N_{\vec{k}s}=a^{\dagger}_{\vec{k}s}a_{\vec{k}s}$ is the number-density operator in the second-quantized form, $a^{\dagger}_{\vec{k}s}$ and $a_{\vec{k}s}$ being the creation and annihilation operators. Choquard[5] has rigorously deduced expression (1) for a three-dimensional lattice. Recently Hardy[6] has given a systematic derivation of the energy-flux operator for a three-dimensional lattice with imperfections and anharmonic forces. The treatment is based on the general expression for the energy flux in terms of the particle variables, which are valid for all phases of matter. He has shown that the expression (1) corresponds to the diagonal part of the average-energy-flux operator arising from harmonic forces; the total average-energy-flux operator contains some nondiagonal terms even in the harmonic approximation.

In the last few years, the thermal conductivity of an anharmonic crystal has been the subject of considerable investigation by many workers. Schieve and Peterson[7] obtained an expression for the thermal conductivity of a crystal using the correlation-function method. A similar expression has been derived by Deo and Behra[8] for an anharmonic crystal using the double-time-Green's-function technique. In all these studies, the effect of the nondiagonal part of the energy-flux operator to the thermal conductivity has been neglected.

In the present paper we have obtained an expression for the thermal conductivity of an anharmonic Bravais crystal considering the nondiagonal term in the energy-flux operator given by Hardy[6] using the double-time-Green's-function technique. It is shown that there is a finite contribution of the nondiagonal part of the energy flux to the thermal conductivity of an anharmonic crystal. The present approach differs from that of Hardy, Swenson, and Schieve[9] in the sense that they have used a perturbation expansion for the correlation-function formula for the thermal conductivity.

II. GENERAL FORMULATION

We start with the Kubo correlation-function formula for the thermal conductivity, which can be written[10]

$$K=\lim_{\epsilon\to 0}\frac{k_B\beta}{3\Omega}\int_0^{\infty} dt\, e^{-\epsilon t}\int_0^{\beta} d\lambda\, \langle\vec{Q}(0)\cdot\vec{Q}(t+i\hbar\lambda)\rangle , \qquad (2)$$

where k_B is Boltzmann's constant, Ω is the volume of the crystal, $\beta=(k_BT)^{-1}$, T being the absolute temperature, $\vec{Q}(t)$ is the energy-flux operator for the lattice in the Heisenberg representation, and the angular bracket $\langle\cdots\rangle$ indicates the canonical-ensemble average of the expectation value of an operator

$$\langle O\rangle = \mathrm{Tr}(e^{-\beta H}O)/\mathrm{Tr}(e^{-\beta H}) , \qquad (3)$$

where Tr denotes the trace of the expression and H is the Hamiltonian of the system. In the harmonic approximation, the total-energy-flux operator suggested by Hardy[6] is given by

$$\vec{Q}=\vec{Q}_{\mathrm{od}}+\vec{Q}_{\mathrm{ond}} , \qquad (4)$$

where $\vec{Q}_{\mathrm{od}}$ is the diagonal part of the energy-flux operator and is given by Eq. (1), and $\vec{Q}_{\mathrm{ond}}$ represents the nondiagonal part of the energy-flux operator for the harmonic system and contains contributions from the modes with the same wave vector but different polarization directions. The latter in terms of the particle variables is given by

$$\vec{Q}_{\text{ond}} = \frac{1}{2} \sum_{\vec{k}ss', s\neq s'} \hbar\omega_{\vec{k}s}\vec{v}_{\vec{k}ss'}A_{\vec{k}s}B^{\dagger}_{\vec{k}s'} , \tag{5}$$

where

$$A_{\vec{k}s} = (a_{\vec{k}s} + a^{\dagger}_{-\vec{k}s}) = A^{\dagger}_{-\vec{k}s} , \qquad B_{\vec{k}s} = (a_{\vec{k}s} - a^{\dagger}_{-\vec{k}s}) = -B^{\dagger}_{-\vec{k}s} . \tag{6}$$

With the help of Eqs. (1), (4), and (5), the expression (2) for thermal conductivity can be written

$$K = K_{\text{od}} + K_{\text{ond}} , \tag{7}$$

where

$$K_{\text{od}} = \lim_{\epsilon\to 0} \frac{\hbar^2 k_B\beta}{3\Omega} \sum_{\vec{k}s} \sum_{\vec{q}s'} \vec{v}_{\vec{k}s}\cdot\vec{v}_{\vec{q}s'}\omega_{\vec{k}s}\omega_{\vec{q}s'} \times \int_0^{\infty} dt\, e^{-\epsilon t} \int_0^{\beta} d\lambda\, F_{\vec{k}s,\vec{q}s'}(t + i\hbar\lambda) \tag{8}$$

and

$$K_{\text{ond}} = \lim_{\epsilon\to 0} \frac{\hbar^2 k_B\beta}{3\Omega} \sum_{\substack{\vec{k}ss'\\ s\neq s'}} \sum_{\substack{\vec{q}_1 s_1 s_1'\\ s_1\neq s_1'}} \vec{v}_{\vec{k}ss'}\cdot\vec{v}_{\vec{q}_1 s_1 s_1'}\omega_{\vec{k}s}\omega_{\vec{q}_1 s_1} \times \int_0^{\infty} dt\, e^{-\epsilon t} \int_0^{\beta} d\lambda\, F_{\vec{k}ss',\vec{q}_1 s_1 s_1'}(t + i\hbar\lambda) , \tag{9}$$

with

$$F_{\vec{k}s,\vec{q}s'}(t) = \langle a^{\dagger}_{\vec{k}s}(0)a_{\vec{k}s}(0)a^{\dagger}_{\vec{k}s'}(t)\, a_{\vec{q}s'}(t)\rangle \tag{10}$$

and

$$F_{\vec{k}ss',\vec{q}_1 s_1 s_1'}(t) = \langle A_{\vec{k}s}(0)\, B^{\dagger}_{\vec{k}s'}(0)A_{\vec{q}_1 s_1}(t)B^{\dagger}_{\vec{q}_1 s_1'}(t)\rangle . \tag{11}$$

The first term in Eq. (7) describes the contribution of the diagonal part of the thermal flux to the thermal conductivity, and the second term corresponds to the nondiagonal contribution.

Equations (8) and (9) show that the evaluation of the thermal conductivity involves the calculation of the correlation functions (10) and (11). This can be evaluated by several techniques. Here we use the double-time-Green's-function technique as illustrated by Zubarev.[11] The method of thermodynamic Green's functions has recently been proved to be very useful in the evaluation of correlation functions and the discussion of various solid-state phenomena. The complexity of the problem is considerably simplified if the two-particle correlation function is decoupled according to the scheme[12,13]

$$\langle abcd\rangle = \langle ab\rangle\langle cd\rangle + \langle ac\rangle\langle bd\rangle + \langle ad\rangle\langle bc\rangle . \tag{12}$$

In Eqs. (8) and (9) only correlation functions with different time arguments contribute to the conductivity. Using the above decoupling scheme, expressions (10) and (11) become

$$F_{\vec{k}s,\vec{q}s'}(t) = \langle a^{\dagger}_{\vec{k}s}(0)a_{\vec{q}s'}(t)\rangle\langle a_{\vec{k}s}(0)a^{\dagger}_{\vec{q}s'}(t)\rangle , \tag{13}$$

$$F_{\vec{k}ss',\vec{q}_1 s_1 s_1'}(t) = \langle A_{\vec{k}s}(0)\, B^{\dagger}_{\vec{q}_1 s_1'}(t)\rangle\langle B^{\dagger}_{\vec{k}s}(0)A_{\vec{q}_1 s_1}(t)\rangle + \langle A_{\vec{k}s}(0)A_{\vec{q}_1 s_1}(t)\rangle\langle B^{\dagger}_{\vec{k}s}(0)B^{\dagger}_{\vec{q}_1 s_1'}(t)\rangle . \tag{14}$$

III. GREEN'S FUNCTION AND HAMILTONIAN

We define the one-particle, retarded Green's function for the system as[11]

$$G_{\vec{k}s,\vec{k}'s'}(t-t') = \langle\langle A_{\vec{k}s}(t);\, A^{\dagger}_{\vec{k}'s'}(t')\rangle\rangle = -i\theta(t-t')\langle [A_{\vec{k}s}(t),\, A^{\dagger}_{\vec{k}'s'}(t')]\rangle , \tag{15}$$

where $\theta(t)$ is the Heavyside step function having the property $\theta(t)=1$ if $t>0$ and $\theta(t)=0$ if $t<0$. The one-particle correlation function $\langle A^{\dagger}_{\vec{k}'s'}(t')A_{\vec{k}s}(t)\rangle$ can be written

$$F_{\vec{k}'s',\vec{k}s}(t,\ t') = \langle A^{\dagger}_{\vec{k}'s'}(t')A_{\vec{k}s}(t)\rangle = \int_{-\infty}^{\infty} d\omega\, J_{\vec{k}s,\vec{k}'s'}(\omega)\, e^{-i\omega(t-t')} , \tag{16}$$

where $J_{\vec{k}s,\vec{k}'s'}(\omega)$ is the spectral-density function. The relationship between the spectral-density function and the Green's function is

$$J_{\vec{k}s,\vec{k}'s'}(\omega) = \frac{i}{e^{\beta\hbar\omega}-1}\left[G_{\vec{k}s,\vec{k}'s'}(\omega+i\epsilon) - G_{\vec{k}s,\vec{k}'s'}(\omega-i\epsilon)\right] , \tag{17}$$

$G_{\vec{k}s,\vec{k}'s'}(\omega)$ being the Fourier transform of the one-particle Green's function.

For the Hamiltonian, we consider a Bravais crystal containing N atoms, each of mass M. The potential energy can be expanded in terms of the atomic displacements from their equilibrium positions. Retaining cubic and quartic terms in the expansion of potential energy and expressing the atomic displacements and momentum vectors in terms of the phonon creation $(a^{\dagger}_{\vec{k}s})$ and annihilation $(a_{\vec{k}s})$ operators in the usual manner, the Hamiltonian of an anharmonic crystal in the second-quantized form can be written

$$\begin{aligned} H = {} & \sum_{\vec{k}s} \hbar\omega_{\vec{k}s}(a^{\dagger}_{\vec{k}s}a_{\vec{k}s} + \tfrac{1}{2}) \\ & + \sum_{\vec{k}_1 s_1}\sum_{\vec{k}_2 s_2}\sum_{\vec{k}_3 s_3} \hbar V^{(3)}(\vec{k}_1 s_1,\ \vec{k}_2 s_2,\ \vec{k}_3 s_3)A_{\vec{k}_1 s_1}A_{\vec{k}_2 s_2}A_{\vec{k}_3 s_3} \\ & + \sum_{\vec{k}_1 s_1}\sum_{\vec{k}_2 s_2}\sum_{\vec{k}_3 s_3}\sum_{\vec{k}_4 s_4} \hbar V^{(4)}(\vec{k}_1 s_1,\ \vec{k}_2 s_2,\ \vec{k}_3 s_3,\ \vec{k}_4 s_4) \times A_{\vec{k}_1 s_1}A_{\vec{k}_2 s_2}A_{\vec{k}_3 s_3}A_{\vec{k}_4 s_4} . \end{aligned} \tag{18}$$

Here the coefficients $V^{(3)}$ and $V^{(4)}$ are the Fourier transforms of the third- and fourth-order atomic force constants. They are completely symmetric in the indices $\vec{k}s$ and are given by[14]

$$V^{(3)}(\vec{k}_1 s_1,\ \vec{k}_2 s_2,\ \vec{k}_3 s_3) = \frac{1}{6\times 2^{3/2}N^{1/2}}\frac{\hbar^{1/2}}{(\omega_{\vec{k}_1 s_1}\omega_{\vec{k}_2 s_2}\omega_{\vec{k}_3 s_3})^{1/2}}$$

$$\times\phi(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3)\Delta(\vec{k}_1+\vec{k}_2+\vec{k}_3) \quad (19)$$

and

$$V^{(4)}(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3,\ \vec{k}_4s_4) = \frac{1}{2^2\times 24N}\frac{\hbar}{(\omega_{\vec{k}_1s_1}\omega_{\vec{k}_2s_2}\omega_{\vec{k}_3s_3}\omega_{\vec{k}_4s_4})^{1/2}} \times\phi(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3,\ \vec{k}_4s_4) \times\Delta(\vec{k}_1+\vec{k}_2+\vec{k}_3+\vec{k}_4)\ , \quad (20)$$

with

$$\phi(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3)=\sum_{i,j,k}\frac{\phi_{ijk}}{M^{3/2}}\vec{e}(\vec{k}_1s_1)\vec{e}(\vec{k}_2s_2)\vec{e}(\vec{k}_3s_3) \times\exp[i(\vec{k}_1\cdot\vec{R}_i+\vec{k}_2\cdot\vec{R}_j+\vec{k}_3\cdot\vec{R}_k)]\ , \quad (21)$$

$$\phi(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3,\ \vec{k}_4s_4)=\sum_{i,j,k,l}\frac{\phi_{ijkl}}{M^2} \times\vec{e}(\vec{k}_1s_1)\vec{e}(\vec{k}_2s_2)\vec{e}(\vec{k}_3s_3)\vec{e}(\vec{k}_4s_4) \times\exp[i(\vec{k}_1\cdot\vec{R}_i+\vec{k}_2\cdot\vec{R}_j+\vec{k}_3\cdot\vec{R}_k+\vec{k}_4\cdot\vec{R}_l)]\ , \quad (22)$$

where ϕ_{ijk} and ϕ_{ijkl} are the third- and fourth-order force constants of the crystal and $\Delta(\vec{k})=1$ if $\vec{k}=0$ or a reciprocal-lattice vector, and zero otherwise.

The correlation functions appearing in Eqs. (13) and (14) are the integral over the Fourier transforms of their respective Green's functions. To evaluate them we introduce the following one-particle Green's functions:

$$G^{(1)}_{\vec{k}s,\vec{q}s'}(t-t')=\langle\langle a_{\vec{k}s}(t);\ a_{\vec{q}s'}(t')\rangle\rangle\ , \quad (23a)$$

$$G^{(2)}_{\vec{k}s,\vec{q}_1s_1}(t-t')=\langle\langle A_{\vec{k}s}(t);\ A_{\vec{q}_1s_1}(t')\rangle\rangle\ , \quad (23b)$$

$$G^{(3)}_{\vec{k}s',\vec{q}_1s_1'}(t-t')=\langle\langle B^\dagger_{\vec{k}s'}(t);\ B^\dagger_{\vec{q}_1s_1}(t')\rangle\rangle\ , \quad (23c)$$

$$G^{(4)}_{\vec{k}s,\vec{q}_1s_1'}(t-t')=\langle\langle A_{\vec{k}s}(t);\ B^\dagger_{\vec{q}_1s_1'}(t')\rangle\rangle\ . \quad (23d)$$

The equation of motion for the Green's function (23a) is

$$i\hbar\frac{d}{dt}G^{(1)}_{\vec{k}s,\vec{q}s'}(t-t')=\hbar\delta(t-t')\langle[a_{\vec{k}s}(t),\ a^\dagger_{\vec{q}s'}(t')]\rangle + \langle\langle[a_{\vec{k}s}(t),\ H(t)];\ a^\dagger_{\vec{q}s'}(t')\rangle\rangle\ ,$$

which for the Hamiltonian (18) becomes

$$i\frac{d}{dt}G^{(1)}_{\vec{k}s,\vec{q}s'}(t-t')=\delta(t-t')\delta_{\vec{k}\vec{q}'}\delta_{ss'}+\omega_{\vec{k}s}G^{(1)}_{\vec{k}s,\vec{q}s'}(t-t') +3\sum_{\vec{k}_1s_1}\sum_{\vec{k}_2s_2}V^{(3)}(\vec{k}_1s_1,\ \vec{k}_2s_2,\ -\vec{k}s) \times\langle\langle A_{\vec{k}_1s_1}(t)A_{\vec{k}_2s_2}(t);\ a^\dagger_{\vec{q}s'}(t')\rangle\rangle +4\sum_{\vec{k}_1s_1}\sum_{\vec{k}_2s_2}\sum_{\vec{k}_3s_3}V^{(4)}(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3,\ -\vec{k}s) \times\langle\langle A_{\vec{k}_1s_1}(t)A_{\vec{k}_2s_2}(t)A_{\vec{k}_3s_3}(t);\ a^\dagger_{\vec{q}s'}(t)\rangle\rangle, \quad (24)$$

where $\delta_{ss'}$ is the Kronecker delta. By taking the Fourier transform and using the decoupling scheme (12), we obtain

$$(\omega-\omega_{\vec{k}s})G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega)=\frac{1}{2\pi}\delta_{\vec{k}\vec{q}}\delta_{ss'} +3\sum_{\vec{k}_1s_1}\sum_{\vec{k}_2s_2}V^{(3)}(\vec{k}_1s_1,\ \vec{k}_2s_2,\ -\vec{k}s)\Gamma^{(1)}_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{q}s'}(\omega) +12\sum_{\vec{k}_1s_1}\sum_{\vec{k}_2s_2}\sum_{\vec{k}_3s_3}V^{(4)}(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \vec{k}_3s_3,\ -\vec{k}s) \times N_{\vec{k}_2s_2}G_{\vec{k}_1s_1,\vec{q}s'}(\omega)\ , \quad (25)$$

with

$$\Gamma^{(1)}_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{q}s'}(\omega)=\langle\langle A_{\vec{k}_1s_1}(t)A_{\vec{k}_2s_2}(t);\ a_{\vec{q}s'}(t')\rangle\rangle_\omega =F(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \omega) \times\sum_{\vec{q}_1s_1}V^{(3)}(-\vec{k}_1s_1,\ -\vec{k}_2s_2,\ \vec{q}_1s_1)G_{\vec{q}_1s_1,\vec{q}s'}(\omega)\ , \quad (26)$$

where

$$F(\vec{k}_1s_1,\ \vec{k}_2s_2,\ \omega)=6(N_1+N_2)\frac{\omega_1+\omega_2}{\omega^2-(\omega_1+\omega_2)^2} +6(N_2-N_1)\frac{\omega_1-\omega_2}{\omega^2-(\omega_1-\omega_2)^2} +6(N_1'+N_2')\left(\frac{\omega}{\omega^2-(\omega_1+\omega_2)^2}-\frac{\omega}{\omega^2-(\omega_1-\omega_2)^2}\right), \quad (27)$$

with

$$N_{\vec{k}s}=\langle A^\dagger_{\vec{k}s}A_{\vec{k}s}\rangle\ ,\qquad N_1=\langle B_{\vec{k}_1s_1}A^\dagger_{\vec{k}_1s_1}\rangle\ , \qquad N_2'=\langle A^\dagger_{\vec{k}_2s_2}B_{\vec{k}_2s_2}\rangle\ . \quad (28)$$

If we substitute Eq. (26) in Eq. (25), we finally obtain for the one-particle Green's function

$$G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega)=\frac{\delta_{\vec{k}\vec{q}}\delta_{ss}}{2\pi[\omega-\omega_{\vec{k}s}-M_{\vec{k}s}(\omega)]}\ , \quad (29)$$

where

$$M_{\vec{k}s}(\omega)=3\sum_{\vec{k}_1s_1}\sum_{\vec{k}_2s_2}|V^{(3)}(\vec{k}_1s_1,\vec{k}_2s_2,\ -\vec{k}s)|^2 \times F(\vec{k}_1s_1,\vec{k}_2s_2,\omega) +12\sum_{\vec{k}_1s_1}V^{(4)}(\vec{k}_1s_1,\ -\vec{k}_1s_1,\vec{k}s,\ -\vec{k}s)N_{\vec{k}_1s_1}\ . \quad (30)$$

$M_{\vec{k}s}(\omega)$ gives the effect of perturbation on the self-energy of one particle. Explicit expression for $M_{\vec{k}s}(\omega)$ can be obtained by writing

$$M_{\vec{k}s}(\omega+i\epsilon)=\Delta_{\vec{k}s}(\omega)-i\Gamma_{\vec{k}s}(\omega)\ . \quad (31)$$

The real part of $M_{\vec{k}s}(\omega+i\epsilon)$ represents the change in the value of the frequency of $\vec{k}$th mode in the sth branch, while the imaginary part gives half-width of the response function. From Eqs. (30) and (31), we finally obtain

$$\Delta_{\vec{k}s}(\omega)=18\,\mathcal{P}\sum_{\vec{k}_1 s_1}\sum_{\vec{k}_2 s_2}\left|V^{(3)}(\vec{k}_1 s_1,\vec{k}_2 s_2,-\vec{k}s)\right|^2 \times\left((N_1+N_2)\frac{\omega_1+\omega_2}{\omega^2-(\omega_1+\omega_2)^2}+(N_2-N_1)\frac{\omega_1-\omega_2}{\omega^2-(\omega_1-\omega_2)^2}\right)+12\sum_{\vec{k}_1 s_1}V^{(4)}(\vec{k}_1 s_1,-\vec{k}_1 s_1,\vec{k}s,-\vec{k}s)N_{\vec{k}_1 s_1} \tag{32}$$

and

$$\Gamma_{\vec{k}s}(\omega)=18\pi\epsilon(\omega)\sum_{\vec{k}_1 s_1}\sum_{\vec{k}_2 s_2}\left|V^{(3)}(-\vec{k}s,\vec{k}_1 s_1,\vec{k}_2 s_2)\right|^2 \times\left[(N_1+N_2)(\omega_1+\omega_2)\,\delta(\omega^2-(\omega_1+\omega_2)^2)+(N_2-N_1)(\omega_1-\omega_2)\,\delta(\omega^2-(\omega_1-\omega_2)^2)\right], \tag{33}$$

in which $\mathcal{P}$ stands for principal part and

$$\epsilon(\omega)=1 \quad \text{for } \omega>0$$
$$=-1 \quad \text{for } \omega<0.$$

With this result Eq. (29) reduces to

$$G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega)=\frac{\delta_{\vec{k}\vec{q}}\,\delta_{ss'}}{2\pi[\omega-\epsilon_{\vec{k}s}(\omega)+i\Gamma_{\vec{k}s}(\omega)]}, \tag{34}$$

where $\epsilon_{\vec{k}s}(\omega)=\omega_{\vec{k}s}+\Delta_{\vec{k}s}(\omega)$ is the perturbed frequency of the kth mode.

Similarly, if we proceed with the equation of motion of Green's functions (23b)–(23d), and follow the procedure as used above, we obtain

$$G^{(2)}_{\vec{k}s,\vec{q}_1 s_1}(\omega)=\frac{\omega_{\vec{k}s}\,\delta_{\vec{k}-\vec{q}_1}\,\delta_{ss_1}}{\pi[\omega^2-\eta^2(\vec{k}s)+2i\omega_{\vec{k}s}\Gamma_{\vec{k}s}(\omega)]}, \tag{35}$$

$$G^{(3)}_{\vec{k}s';\vec{q}_1 s_1'}(\omega)=-\frac{\omega_{\vec{k}s'}\,\delta_{\vec{k}-\vec{q}_1}\,\delta_{s's_1'}}{\pi[\omega^2-\eta^2(\vec{k}s)+2i\,\omega_{\vec{k}s'}\Gamma_{\vec{k}s'}(\omega)]}, \tag{36}$$

$$G^{(4)}_{\vec{k}s,\vec{q}_1 s_1'}(\omega)=\frac{\omega\,\delta_{\vec{k}-\vec{q}_1}\,\delta_{ss_1'}}{\pi[\omega^2-\eta^2(\vec{k}s)+2i\omega_{\vec{k}s}\Gamma_{\vec{k}s}(\omega)]}, \tag{37}$$

where

$$\eta^2(\vec{k}s)=\omega^2_{\vec{k}s}+2\omega_{\vec{k}s}\Delta_{\vec{k}s}(\omega).$$

Having formulated the Green's functions, we can obtain the spectral-density function by using the relation (17), and the correlation function from Eq. (16).

IV. THERMAL CONDUCTIVITY

We evaluate separately the diagonal and nondiagonal contributions to the thermal conductivity. Substituting the values of the correlation functions occurring in Eq. (13) with the help of (16), (17), and (34) and performing the integration over t and λ, the diagonal contribution to the thermal conductivity is given by

$$K_{\rm od}=\lim_{\epsilon\to 0}\frac{i\hbar k_B\beta}{3\Omega}\sum_{\vec{k}s}\sum_{\vec{q}s'}\vec{v}_{\vec{k}s}\cdot\vec{v}_{\vec{q}s'}\,\omega_{\vec{k}s}\,\omega_{\vec{q}s'} \times\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}d\omega_1\,d\omega_2 \times\frac{e^{\beta\hbar\omega_1}-e^{\beta\hbar\omega_2}}{(e^{\beta\hbar\omega_1}-1)(e^{\beta\hbar\omega_2}-1)(\omega_1-\omega_2)(\omega_1-\omega_2-i\epsilon)} \times[G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega_1+i\epsilon)-G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega_1-i\epsilon)] \times[G^{(1)}_{\vec{q}s',\vec{k}s}(\omega_2+i\epsilon)-G^{(1)}_{\vec{q}s',\vec{k}s}(\omega_2-i\epsilon)]. \tag{38}$$

Interchanging ω_1 and ω_2 and using the relation

$$(\omega_1-\omega_2-i\epsilon)^{-1}-(\omega_1-\omega_2+i\epsilon)^{-1}=2\pi i\,\delta(\omega_1-\omega_2), \tag{39}$$

Eq. (38) reduces to

$$K_{\rm od}=\frac{-\hbar^2\pi k_B\beta^2}{3\Omega}\lim_{\epsilon\to 0}\sum_{\vec{k}s}\sum_{\vec{q}s'}\vec{v}_{\vec{k}s}\cdot\vec{v}_{\vec{q}s'}\,\omega_{\vec{k}s}\,\omega_{\vec{q}s'} \times\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \times[G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega+i\epsilon)-G^{(1)}_{\vec{k}s,\vec{q}s'}(\omega-i\epsilon)] \times[G^{(1)}_{\vec{q}s',\vec{k}s}(\omega+i\epsilon)-G^{(1)}_{\vec{q}s',\vec{k}s}(\omega-i\epsilon)]. \tag{40}$$

Substituting the value of $G^{(1)}(\omega)$ from Eq. (34), we obtain

$$K_{\rm od}=\frac{\hbar^2 k_B\beta^2}{3\Omega\pi}\sum_{\vec{k}s}v^2_{\vec{k}s}\,\omega^2_{\vec{k}s} \times\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\frac{\Gamma^2_{\vec{k}s}(\omega)}{\{[\omega-\epsilon_{\vec{k}s}(\omega)]^2+\Gamma^2_{\vec{k}s}(\omega)\}^2}. \tag{41}$$

For small values of $\Gamma_{\vec{k}s}(\omega)$, the integrand in Eq. (41) is peaked around $\omega\simeq\epsilon_{\vec{k}s}$ and the integration gives the thermal conductivity as

$$K_{\rm od}=\frac{\hbar^2 k_B\beta^2}{3\Omega}\sum_{\vec{k}s}v^2_{\vec{k}s}\,\omega^2_{\vec{k}s}\,\frac{e^{\beta\hbar\epsilon_{\vec{k}s}}}{(e^{\beta\hbar\epsilon_{\vec{k}s}}-1)^2}\,\frac{1}{2\Gamma_{\vec{k}s}}. \tag{42}$$

Equation (42) gives the familiar expression for the relaxation time of kinetic theory for thermal conductivity as obtained by the Boltzmann transport equation and discussed by Carruthers[2] and Klemens.[3]

The nondiagonal contribution to the thermal conductivity can be obtained in the similar way. Using Eqs. (14), (16), and (17) in (9), $K_{\rm ond}$ can be written as

$$K_{\rm ond}=K'_{\rm ond}+K''_{\rm ond}, \tag{43}$$

where

$$K'_{\mathrm{ond}}=-\frac{\hbar^2 k_B \beta^2 \pi}{12\Omega}\sum_{\substack{\vec{k}ss'\\ s\neq s'}}\sum_{\substack{\vec{q}_1 s_1 s_1'\\ s_1\neq s_1'}}\vec{v}_{\vec{k}ss'}\cdot\vec{v}_{\vec{q}_1 s_1 s_1'}\,\omega_{\vec{k}s}\,\omega_{\vec{q}_1 s_1}\times\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

$$\times\left[G^{(2)}_{\vec{k}s,\vec{q}_1 s_1}(\omega+i\epsilon)-G^{(2)}_{\vec{k}s,\vec{q}_1 s_1}(\omega-i\epsilon)\right]\times\left[G^{(3)}_{\vec{k}s',\vec{q}_1 s_1'}(\omega+i\epsilon)-G^{(3)}_{\vec{k}s',\vec{q}_1 s_1'}(\omega-i\epsilon)\right]. \quad (44)$$

With the help of Eqs. (35) and (36), Eq. (44) becomes

$$K'_{\mathrm{ond}}=-\frac{4\hbar^2 k_B \beta^2}{3\pi\Omega}\sum_{\substack{\vec{k}ss'\\ s\neq s'}}\sum_{\substack{\vec{q}_1 s_1 s_1'\\ s_1\neq s_1'}}\vec{v}_{\vec{k}ss'}\cdot\vec{v}_{\vec{q}_1 s_1 s_1'}\,\omega_{\vec{k}s}\,\omega_{\vec{q}_1 s_1}\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\omega^2_{\vec{k}s}\,\omega^2_{\vec{k}s'}\,\delta_{\vec{k}-\vec{q}_1}\,\delta_{s's_1'}\,\delta_{ss_1}$$

$$\times\frac{\Gamma_{\vec{k}s}(\omega)\,\Gamma_{\vec{k}s'}(\omega)}{\{[\omega^2-\eta^2(\vec{k}s)]^2+4\omega^2_{\vec{k}s}(\omega)\,\lambda\}\{[\omega^2-\eta^2(\vec{k}s')]^2+4\omega^2_{\vec{k}s'}\,\Gamma^2_{\vec{k}s'}(\omega)\}}=-\frac{4\hbar^2 k_B\beta^2}{3\pi\Omega}\sum_{\substack{\vec{k}ss'\\ s\neq s'}}\vec{v}_{\vec{k}ss'}\cdot\vec{v}_{-\vec{k}ss'}\,\omega_{\vec{k}s}\,\omega_{-\vec{k}s'}$$

$$\times\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\frac{\omega^2_{\vec{k}s}\,\omega^2_{\vec{k}s'}\,\Gamma_{\vec{k}s}(\omega)\,\Gamma_{\vec{k}s'}(\omega)}{\{[\omega^2-\eta^2(\vec{k}s)]^2+4\omega^2_{\vec{k}s}\Gamma^2_{\vec{k}s}(\omega)\}\{[\omega^2-\eta^2(\vec{k}s')]^2+4\omega^2_{\vec{k}s'}\Gamma^2_{\vec{k}s}(\omega)\}}\,. \quad (45)$$

If we use the symmetry relations

$$\vec{v}_{\vec{k}ss'}=-\vec{v}_{-\vec{k}ss'},\quad \omega_{\vec{k}s}=\omega'_{-\vec{k}s}\,,$$

Eq. (45) can be rewritten

$$K'_{\mathrm{ond}}=\frac{4}{3}\,\frac{\hbar^2 k_B\beta^2}{\pi\Omega}\sum_{\substack{\vec{k}ss'\\ s\neq s'}}\vec{v}^{\,2}_{\vec{k}ss'}\,\omega^3_{\vec{k}s}\,\omega^3_{\vec{k}s'}\int_{-\infty}^{\infty}d\omega\,\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\frac{\Gamma_{\vec{k}s}(\omega)\,\Gamma_{\vec{k}s'}(\omega)}{\{[\omega^2-\eta^2(\vec{k}s)]^2+4\omega^2_{\vec{k}s}\Gamma^2_{\vec{k}s}(\omega)\}\{[\omega^2-\eta^2(\vec{k}s')]^2+4\omega^2_{\vec{k}s'}\,\Gamma^2_{\vec{k}s'}(\omega)\}}\,. \quad (46)$$

Similarly, we have

$$K''_{\mathrm{ond}}=\frac{4}{3}\,\frac{\hbar^2 k_B\beta^2}{\pi\Omega}\sum_{\substack{\vec{k}ss'\\ s\neq s'}}\vec{v}^{\,2}_{\vec{k}ss'}\,\omega^2_{\vec{k}s}\,\omega^2_{\vec{k}s'}\int_{-\infty}^{\infty}d\omega\,\frac{\omega^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\frac{\Gamma_{\vec{k}s}(\omega)\,\Gamma_{\vec{k}s'}(\omega)}{\{[\omega^2-\eta^2(\vec{k}s)]^2+4\omega^2_{\vec{k}s}\Gamma^2_{\vec{k}s}(\omega)\}\{[\omega^2-\eta^2(\vec{k}s')]^2+4\omega^2_{\vec{k}s'}\,\Gamma^2_{\vec{k}s'}(\omega)\}}\,. \quad (47)$$

Expressions (46) and (47) show that the nondiagonal contribution to the thermal conductivity comes from modes of different polarization directions. These equations give corrections to the Boltzmann equation for the thermal conductivity. When the anharmonic energy is small, one expects the diagonal element of the energy-flux operator to give the major contribution to the transport of energy. In the harmonic approximation, when the cubic and quartic anharmonic terms are left out in the Hamiltonian (18), the nondiagonal part of the energy-flux operator leads to zero contribution to the thermal conductivity. Hardy[6] has argued, based on classical treatment, that the contribution of $\vec{Q}_{\mathrm{ond}}$ to the transport of energy is in general negligible in comparison to that of the diagonal term $\vec{Q}_{\mathrm{od}}$. Expressing the phonon operators in Eq. (5) in terms of the normal-mode variables $q_{\vec{k}s}$ and $p_{\vec{k}s}$ and treating the latter as classical variables, expression (5) becomes an oscillatory function of terms whose frequencies are the sum and difference of $\omega_{\vec{k}s}$ and $\omega_{\vec{k}s'}$. As a result, the average of the flux over many oscillations becomes negligibly small.

ACKNOWLEDGMENTS

The authors are thankful to the Council of Scientific and Industrial Research, New Delhi, for financial support and to Professor Vachaspati and Dr. K. S. Singwi for encouragement. The work was partly supported by the Department of Atomic Energy.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Stress-Induced Band Gap and Related Phenomena in Gray Tin†

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The conductivity and low-field Hall coefficient of high-purity ($N_D - N_A \sim 5 \times 10^{14}$ cm^{-3}) and lightly doped ($2 \times 10^{15} \leq N_D \leq 2 \times 10^{17}$ cm^{-3}) n-type gray tin subjected to oriented uniaxial compressions have been measured between 1.4 and 100 °K. Stress (χ) exceeding 3×10^9 dyn/cm^2 was achieved in both [001] and [111] orientations. Density-of-states expressions are developed to account for the severe band anisotropies imposed by the strain in the normally degenerate Γ_8^+ conduction and valence bands, and these are employed to determine the band splittings at $\vec{k}=0$ from the Hall coefficient of the high-purity samples above 15 °K. Shear deformation potentials of $b = -2.3 \pm 0.5$ eV and $d \simeq -4.1$ eV are obtained by this procedure. The Hall coefficient of three high-purity samples below 10 °K is analyzed to find the stress-dependent impurity-ionization energy $E_D(\chi)$, and from the measured $E_D(\chi)$ for the highest-purity sample an independent determination of $b = -2.4$ eV is obtained if $E_D(\chi)$ is interpreted as reflecting donor-to-conduction-band activation. However, the measured $E_D(\chi)$ for this sample is also found to be consistent with activation from the donor ground state into a D^- band. The stress dependence of the impurity mobility in two of these samples is explained in terms of Sladek's model for exchange jumping between filled and unfilled impurity sites. The piezoresistance of lightly doped samples is attributed to the increased effectiveness of ionized impurity scattering caused by a stress enhancement of the Γ_8^+ density-of-states mass.

I. INTRODUCTION

The salient feature of the Groves-Paul band-structure model of gray tin is the degeneracy of the Γ_8^+ conduction and valence bands at $\vec{k}=0$.[1] Like the degenerate valence bands in other diamond structures these bands arise from atomic p orbitals, but because of the placement of the Γ_7^- state below Γ_8^+ in gray tin and their interaction via $\vec{k}\cdot\vec{p}$, the curvature of the light-mass valence band is inverted. The thermal-energy gap is then fixed identically at zero. Since this degeneracy is ultimately a consequence of the cubic symmetry of the diamond structure, the zero gap remains unaffected by the application of hydrostatic pressure.[2] However, the presence of a directed perturbation in the lattice structure, such as a uniaxial strain, reduces the lattice symmetry and thereby destroys the degeneracy at $\vec{k}=0$.[3,4] With the correct sign of the strain, a direct gap will be created, yielding a new small-band-gap semiconductor in which the intrinsic carrier density is governed by the magnitude of the applied stress.

In this paper we report measurements of the conductivity and low-field Hall coefficient $R(0)$ of high-purity ($N_D - N_A \sim 5 \times 10^{14}$ cm^{-3}) and intermediate-purity gray-tin single crystals subjected to [001] and [111] uniaxial compressions at temperatures between 1.4 and 100 °K. Stress removes the degeneracy at $\vec{k}=0$, but because the strain-induced admixture of higher bands (primarily Γ_7^-) depends on the angle between $\vec{k}$ and the strain axis, the split energy bands become anisotropic. Therefore, expressions which incorporate these anisotropies are developed for the carrier densities in the [001]- and [111]-strained Γ_8^+ bands. These expressions are used to evaluate the energy splitting at $\vec{k}=0$ and the corresponding shear deformation potentials from the intrinsic Hall coefficient of high-purity samples.

The development of an energy gap between the normally degenerate conduction and valence bands permits the establishment of energetically isolated impurity states in material of sufficient purity. For the highest-purity samples studied here, the existence of these states is inferred from the structure which develops in the high-stress low-temperature Hall coefficient and from the pronounced