

Foundations of the Callaway Theory of Thermal Conductivity

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The equation derived by Peierls for the occupation numbers N_q of phonon states with wave vector \mathbf{q} and appropriate polarization is linearized to give a master equation for the deviations $n_q \equiv N_q - N_q^0$ from equilibrium. This master equation, with transition probabilities calculated from first-order time-dependent perturbation theory, is then compared term by term with the linearized form of an approximate master equation proposed by Callaway. The latter assumes that the effects of normal and umklapp processes can be represented by two relaxation frequencies, τ_N^{-1} and τ_r^{-1} , respectively, which are both proportional to q^2 . This assumption is contradicted by the present analysis, which shows that the condition that the solution of the Callaway equation should also satisfy the Peierls equation in the case of steady-state heat flow leads to τ_N^{-1} proportional to q in first approximation. Furthermore, the Callaway equation contains nonzero transition probabilities for a great many phonon processes which are absent from the Peierls equation. Thus, while Callaway's equation, with a modified τ_N , can indeed give a good approximation to the phonon occupation numbers in the steady state, it does not describe the approach to that state from an arbitrary initial distribution. These conclusions are found to remain true when boundary and point-defect scattering are included, in addition to three-phonon processes. A first approximation to the wave number and temperature dependence of the corresponding contribution to the Callaway relaxation times is given for each scattering mechanism.

1. INTRODUCTION

IN the language in which the states of a crystal are approximated by eigenstates of a Hamiltonian of the perfect crystal quadratic in the displacements of the atoms from their equilibrium positions, we can speak of a distribution of phonons, of which N_q have wave vector \mathbf{q} . Each of these phonons is polarized, so that a polarization index must be added to distinguish among phonons of the same wave vector and different directions of vibration. This index will be understood and not written down explicitly.

The anharmonic terms in the Hamiltonian, plus perturbations due to any defects present in the lattice, induce transitions between phonon states, with transition probability $A_{\mathbf{q}\mathbf{q}'}$ per unit time, which can be calculated from time-dependent perturbation theory. Thus, we can write down a master equation,

$$\partial N_q / \partial t = \sum_{\mathbf{q}'} A_{\mathbf{q}\mathbf{q}'} (N_{\mathbf{q}'} - N_{\mathbf{q}'}^0) + \mathbf{C}_q \cdot \nabla T (\partial N_q / \partial T), \quad (1)$$

where N_q^0 is the equilibrium distribution, and the last term, with C_q the group velocity for phonons of wave vector \mathbf{q} , is the "drift" term induced by the temperature gradient. The calculation of a first approximation to $A_{\mathbf{q}\mathbf{q}'}$, and a comparison of the result with an intuitive approximation proposed by Callaway, are the principle aims of the present paper.

Equation (1) is difficult to solve when $A_{\mathbf{q}\mathbf{q}'}$ is non-diagonal, and so it has been approximated by a Boltzmann equation¹ with a single relaxation time. The latter is successful at very low temperatures, but it fails by a small amount near the conductivity maximum, and so an effort was made by Callaway to improve it.²

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¹ Compare P. Carruthers, *Rev. Mod. Phys.* **33**, 92 (1961), especially pp. 102 ff.

² J. Callaway, *Phys. Rev.* **113**, 1046 (1959).

This improvement seeks to account explicitly for normal or " N processes" which scatter phonons but do not lead to an equilibrium state. Intuitively, one should be able to represent the effect of N processes by a second relaxation time, $\tau_N(\mathbf{q})$, which tends to cause the occupation numbers N_q to relax to a nonequilibrium distribution. Thus, Callaway² approximates Eq. (1) by

$$\partial N_q / \partial t = (\tau_N)^{-1} (N_q^0(\lambda) - N_q) + (\tau_r)^{-1} (N_q^0 - N_q) + \mathbf{C}_q \cdot \nabla T (\partial N_q^0 / \partial T), \quad (2)$$

where N_q^0 is the Planck equilibrium distribution,

$$N_q^0 = [\exp(\hbar\omega_q/kT) - 1]^{-1} \quad (3)$$

with ω_q the phonon frequency, and $N_q^0(\lambda)$ is a displaced distribution with $\hbar\omega_q$ replaced by $(\hbar\omega_q + \lambda \cdot \mathbf{q})$. $\tau_r(\mathbf{q})$ is attributed entirely to umklapp, or U processes, which, unlike τ_N , do tend to induce equilibrium.

Callaway's approximate master equation leads to a thermal conductivity formula which has been remarkably successful in correlating experimental data, despite the fact that its theoretical foundation is purely intuitive. Therefore, it is of interest to make a detailed examination of the theoretical basis for Eq. (2) and, in particular, to determine whether we can indeed calculate τ_N in such a way as to make Eq. (2) approximate Eq. (1), with $A_{\mathbf{q}\mathbf{q}'}$ determined from perturbation theory. The condition that Eqs. (1) and (2) be identical will be formulated in the next section. We shall then go on to obtain the leading terms in an expansion of $A_{\mathbf{q}\mathbf{q}'}$ in powers of \mathbf{q} and \mathbf{q}' which will make possible a term-by-term comparison of Eqs. (1) and (2) in the limit of small $q \equiv |\mathbf{q}|$. This comparison, in Sec. 4, shows that (1) and (2) may disagree markedly for an arbitrary nonequilibrium state. However, in Sec. 5, it will be seen that

³ Cf., B. K. Agrawal and G. S. Verma, *Physica* **28**, 599 (1962); also, *Phys. Rev.* **128**, 603 (1962).

τ_N can indeed be determined so that (1) and (2) agree in the steady state, although the result differs from Callaway's assumptions about the q dependence of τ_N and τ_r .

Since the emphasis in this discussion is on normal processes, all these calculations will be carried out assuming an infinite, perfect crystal, so that we need consider N and U processes only. Any possible modifications due to boundary and defect scattering will be considered briefly in Sec. 6. Since defects are the dominant scattering mechanism at low temperatures, we shall thus be prepared for a discussion of the experimental success of the Callaway theory, which will be the main subject of Sec. 7.

2. FORMULATION OF PROBLEM

Unlike the master equation, the Callaway approximation (2) appears at first sight to have a diagonal transition probability matrix. In fact, however, the parameter λ is expressible as a linear sum of the deviations

$$n_q \equiv N_q - N_q^0,$$

and this circumstance gives rise to off-diagonal terms.

The form of these off-diagonal terms depends on the explicit form of λ , which Callaway calculates from the condition that N processes cannot change the total momentum. This condition is [Ref. 2, Eq. (13)]

$$\int \frac{1}{\tau_N} [N_q^0(\lambda) - N_q] \mathbf{q} d\mathbf{q} = 0. \tag{4}$$

To solve for λ , we shall make an approximation already implicit in Eq. (1), viz., that squares and products of the deviations n_q can be neglected. Under this approximation

$$N_q^0(\lambda) \cong N_q^0 - \frac{\lambda \cdot \mathbf{q}}{kT} \frac{e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2}. \tag{5}$$

A second approximation made by Callaway is that τ_N , as a function of \mathbf{q} , has isotropic or cubic symmetry, so that terms proportional to factors of the type $\lambda_i q_i q_j$, with $i \neq j$, vanish from the integral in Eq. (4). This approximation is made here with no comment on its validity, since we want to compare Callaway's final result with the master equation, whatever may or may not be said for the assumptions which went into his reasoning. Thus, we substitute Eq. (5) into Eq. (4), assume cubic symmetry, and obtain

$$\lambda = -3kT \sum_q (n_q \mathbf{q} / \tau_N) / \left\{ \sum_q [q^2 e^{\hbar\omega/kT} / (\tau_N \{e^{\hbar\omega/kT} - 1\}^2)] \right\}. \tag{6}$$

When Eq. (6) is substituted into Callaway's equation, the result is an approximate master equation with off-diagonal terms, which may be compared with Eq. (1).

To simplify this comparison, we shall rewrite both (1) and (2) as the sum of a diagonal and nondiagonal part, and devote attention to the latter. Thus, we observe that Eq. (2) can be put in the form,

$$\begin{aligned} \partial N_q / \partial t = & (\tau_N)^{-1} (N_q^0(\lambda) - N_q^0) \\ & - \tau_c^{-1} n_q + \mathbf{C}_q \cdot \nabla T (\partial N_q^0 / \partial T), \end{aligned} \tag{7}$$

where

$$\tau_c^{-1} = \tau_N^{-1} + \tau_r^{-1} \tag{8}$$

is the relaxation time in the diagonal approximation, which neglects the momentum-conserving feature of N processes.

Similarly, we can put with complete generality, subject to a definition of τ_c to be given in the following section:

$$A_{qq'} \equiv A_{qq'}^\dagger - \tau_c^{-1} \delta_{qq'} \tag{9}$$

and then proceed to compare the part of Eq. (1) which involves A^\dagger with the term $\tau_N^{-1} (N_q^0(\lambda) - N_q^0)$ in Eq. (7). If the latter equation is linearized by employing Eqs. (5) and (6), the condition that it be identical with Eq. (1) is

$$\frac{3 \sum_{q'} \{ \mathbf{q} \cdot \mathbf{q}' / [\tau_N(\mathbf{q}) \tau_N(\mathbf{q}')] \} n_{q'}}{\sum_q q^2 \tau_N^{-1} N_q^0 (N_q^0 + 1)} = \sum_{q'} S_{qq'} n_{q'}, \tag{10}$$

where

$$S_{qq'} \equiv A_{qq'}^\dagger / (N_q^0 [N_q^0 + 1]). \tag{11}$$

The remaining problem is to calculate $A_{qq'}^\dagger$ from perturbation theory and then to discuss the circumstances under which Eq. (10), the necessary and sufficient condition for identity of Eqs. (1) and (2), can hold true. In this way, we determine the \mathbf{q} dependence of τ_N . An immediate observation is that Eq. (10) appears to require that

$$S_{qq'} = S_{q'q}.$$

This, in fact, has been demonstrated by Leibfried, who has given the form of the perturbation equation for $\partial N_q / \partial t$ which will be used in the following section to yield expressions for τ_c^{-1} and $A_{qq'}^\dagger$.

3. CALCULATION OF TRANSITION PROBABILITIES

On the assumption that it is sufficient to restrict attention to cubic anharmonic terms in the crystal Hamiltonian, Peierls has calculated a general equation for $\partial N_q / \partial t$ from perturbation theory, which we shall use in the form given by Leibfried [Ref. 4, Eq. (92.11)]. Each term in this equation contains a product of three factors, e.g., $(N_q + 1) N_{q'} (N_{q''} + 1)$, corresponding to a process in which one phonon is created or annihilated and two others, respectively, are annihilated or created. When the equation is linearized, through neglect of terms quadratic and cubic in the deviations n_q from

⁴ G. Leibfried in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1; see Eq. (90.7), p. 296.

equilibrium, these three factors give rise to a term proportional to n_q plus two sums containing summands proportional to $n_{q'}$ and n_{q^*} . Of these, the term proportional to n_q is a diagonal contribution to $A_{qq'}$, which is negative if $n_q > 0$, and so we shall identify this term with $-\tau c^{-1} n_q$. The other terms can then be put in the form $\sum A_{qq'}^\dagger n_{q'}$ where, for isotropic symmetry at least, $A_{qq'}^\dagger$ can be shown to have no nonvanishing diagonal elements. Since the calculation is straightforward but slightly tedious, only the result will be given here, which is:

$$A_{qq'}^\dagger = (4\pi/\hbar^2) \times \sum_{q^*} [D_{q,-q',q^*} \delta(\omega_q - \omega_{q'} + \omega_{q^*}) (N_{q^*}^0 + N_{q^*}^0 + 1) + D_{q,q',q^*} \delta(\omega_q + \omega_{q'} - \omega_{q^*}) (N_{q^*}^0 - N_{q^*}^0) + D_{q,-q',q^*} \delta(\omega_q - \omega_{q'} - \omega_{q^*}) (N_{q^*}^0 - N_{q^*}^0)], \quad (12)$$

$$\tau c^{-1} = (2\pi/\hbar^2) \times \sum_{q',q^*} D_{q,q',q^*} [2\delta(\omega_q - \omega_{q'} + \omega_{q^*}) (N_{q^*}^0 - N_{q^*}^0) + \delta(\omega_q - \omega_{q'} - \omega_{q^*}) (N_{q^*}^0 + N_{q^*}^0 + 1)]. \quad (13)$$

In these equations, the D symbol is defined by

$$D_{q,q',q^*} \equiv |\Phi_{q,q',q^*}|^2,$$

where Φ is a matrix element of the cubic anharmonic potential [Compare Ref. 4, Eq. (91.6)], the form of which will be discussed shortly. It will then be seen, as we shall point out in the next section, that Φ vanishes when $\mathbf{q} = \mathbf{q}'$ and both are longitudinal. This will serve to substantiate the assertion that A^\dagger has no diagonal elements.

A simplification of the factors containing $N_{q^*}^0$ in Eq. (12) is achieved by supposing that we are dealing with phonon frequencies sufficiently low that we can expand the exponential in $N_{q^*}^0$ and keep only linear terms, i.e.,

$$N_{q^*}^0 \cong kT/\omega_{q^*}.$$

This approximation will give the leading term in an expansion of τ_N in powers of q , and that is all that is attempted in the present paper.

A further simplification is imposed by the δ factors in Eqs. (12) and (13), which are the conditions of energy conservation in a three-phonon interaction. Thus, on taking account of the delta in the first term of Eq. (13), we have

$$N_{q^*}^0 - N_{q^*}^0 \cong \hbar^{-1} kT (\omega_{q'} - \omega_{q^*}) / (\omega_{q'} \omega_{q^*}) = \hbar^{-1} kT \omega_q / (\omega_{q'} \omega_{q^*}). \quad (14a)$$

Similarly, in the first term of Eq. (12),

$$N_{q^*}^0 + N_{q^*}^0 + 1 \cong \hbar^{-1} kT \omega_q / (\omega_q \omega_{q^*}). \quad (14b)$$

To proceed further in obtaining a first approximation to the \mathbf{q} dependence of $A_{qq'}^\dagger$, we must know the dispersion relations for ω_q . Since the optical phonons have $C_q \cong 0$, they make a negligible contribution to the ther-

mal conductivity, and so we shall assume that we are dealing exclusively with acoustic phonons, for which $\omega_q \propto q$ as $q \rightarrow 0$. Specifically, we shall make the usual isotropic acoustic approximation

$$\omega_q = cq, \quad (15)$$

where c is the sound velocity, which may be either c_l or c_t , depending on whether \mathbf{q} is longitudinally or transversely polarized. c will be treated here as constant, which should be adequate for calculating the leading terms in the \mathbf{q} dependence of A^\dagger .

Finally, it is necessary to approximate D_{q,q',q^*} , which involves an assumption about the interatomic forces. The assumption made here will be that of central forces, for which [Ref. 4, Eq. (91.16)]

$$\Phi_{q,q',q^*} = \sum_{i,k,l} (2N^{1/2})^{-1} \eta_q \eta_{q'} \eta_{q^*} \epsilon_i(\mathbf{q}) \epsilon^k(\mathbf{q}') \epsilon_l(\mathbf{q}^*) \cdot \delta P^{q+q'+q^*} \sum_n \varphi_{ikl} [\exp(i\mathbf{q} \cdot \mathbf{R}_n) - 1] \times [\exp(i\mathbf{q}' \cdot \mathbf{R}_n) - 1] \cdot [\exp(i\mathbf{q}^* \cdot \mathbf{R}_n) - 1], \quad (16)$$

where N = number of atoms in lattice and the sum over n is taken over all lattice sites $\mathbf{R}_n \cdot \eta_q \equiv [\hbar/(2M\omega_q)]^{1/2}$, with M = atomic mass, and $\epsilon_i(\mathbf{q})$ is the direction cosine in direction i of the polarization of \mathbf{q} .

$$\varphi_{ikl} \equiv \partial^3 \varphi / \partial R_i \partial R_j \partial R_l$$

is the derivative of the pair potential. δ_P is the momentum conservation factor which equals unity if $\mathbf{q} + \mathbf{q}' + \mathbf{q}^*$ is a reciprocal lattice vector and vanishes otherwise.

The leading \mathbf{q} dependence of Φ is obtained by expanding the exponentials in (16) and keeping only the first term in each expansion. This gives $\Phi \propto qq'q^*$, with a proportionality factor depending on the directions and polarization angles of the wave vectors. To estimate this angular factor, we shall replace the sum over R_n with an integral over the volume of the lattice. It will be assumed that the radial distribution function for a cubic or nearly isotropic lattice can be approximated by a spherically-symmetric function $g(r)$. One can then effect a partial integration and obtain

$$\Phi_{q,q',q^*} \cong -i(2N^{1/2})^{-1} \eta_q \eta_{q'} \eta_{q^*} qq'q^* \delta_P \cdot \left\{ (1/105) \int \varphi(g'''r^3 - 3g''r^2 + 3g'r) d\mathbf{r} \times \sum^{(PD)} + (1/30) \int \varphi(g''r^2 + 4g'r) d\mathbf{r} \times \sum^{(PE)} + \int \varphi g d\mathbf{r} \sum^{(P)} \right\} \times \mathbf{e}(\mathbf{q}) \cdot \mathbf{e}^\dagger(\mathbf{q}) \mathbf{e}(\mathbf{q}') \cdot \mathbf{e}^\dagger(\mathbf{q}') \mathbf{e}(\mathbf{q}^*) \cdot \mathbf{e}^\dagger(\mathbf{q}^*). \quad (17)$$

The sum $\sum^{(PD)}$ is taken over all distinct scalar products in which the six vectors \mathbf{e} , \mathbf{e}^\dagger are dotted together in

pairs. The sum $\sum^{(PE)}$ is taken over all permutations of the six vectors such that either (a) all \mathbf{e} vectors stand to the left of all \mathbf{e}^\dagger vectors or (b) each \mathbf{e} vector stands to the left of an \mathbf{e}^\dagger vector into which it is dotted. The sum $\sum^{(P)}$ is the sum over all permutations of the three \mathbf{e}^\dagger vectors.

When all the foregoing approximations are applied to Eq. (12), the quantity $S_{\mathbf{q}\mathbf{q}'}$ defined in Eq. (11) assumes the form,

$$S_{\mathbf{q}\mathbf{q}'} \cong \pm \mathfrak{D}(\mathbf{q}\mathbf{q}') q^2 q'^2, \quad (18)$$

where

$$\mathfrak{D}(\mathbf{q}\mathbf{q}') \equiv \frac{\pi \hbar^2}{4NkTM^3 c^{*2}} [(I_1 \sum^{(PD)} + I_2 \sum^{(PE)} + I_3 \sum^{(P)}) \times \mathbf{e}(\mathbf{q}) \cdot \mathbf{e}^\dagger(\mathbf{q}) \mathbf{e}(\mathbf{q}') \cdot \mathbf{e}^\dagger(\mathbf{q}') \mathbf{e}(\mathbf{q}^*) \cdot \mathbf{e}^\dagger(\mathbf{q}^*)]^2, \quad (19)$$

with $c^* \equiv c(\mathbf{q}^*)$ determined as a function of \mathbf{q}, \mathbf{q}' by the momentum and energy conservation conditions. The integrals $I_1, I_2,$ and I_3 multiplying $\sum^{(PD)}, \sum^{(PE)},$ and $\sum^{(P)}$ are the same ones appearing in Eq. (17). The upper sign in Eq. (18) corresponds to vectors \mathbf{q}, \mathbf{q}' for which the first or third terms on the right in Eq. (12) are nonzero, while the minus sign corresponds to \mathbf{q}, \mathbf{q}' for which a nonzero contribution is obtained from the second term. The δ factors assure that, if a given \mathbf{q}, \mathbf{q}' , are both nonzero, then at most one of the three terms in Eq. (12) can be unequal to zero.

The approximate expression (18) will be used in the following section in making a detailed comparison of corresponding terms in Eq. (10). In this way, we shall be able to make some statements about the conditions under which the Callaway equation approximates the master equation. Then, in Sec. 5, we can obtain a first approximation to the \mathbf{q} dependence of τ_N . At the same time, we shall discuss the \mathbf{q} dependence of τ_e^{-1} given by Eq. (13).

4. COMPARISON OF CORRESPONDING TERMS

The analysis of the preceding section, leading to Eq. (18), has prepared the way for a careful examination of the validity of Eq. (10), which is both necessary and sufficient for the validity of Callaway's approximation to the master equation. The method employed will be to list the range of possible vectors \mathbf{q}' which, for given \mathbf{q} , yield $S_{\mathbf{q}\mathbf{q}'} \neq 0$. For any \mathbf{q}' thus listed, we shall examine whether $S_{\mathbf{q}\mathbf{q}'}$ has the same sign as $\mathbf{q} \cdot \mathbf{q}'$, which is the sign of the corresponding term in the left-hand member of Eq. (10). Having established that most terms in the right-hand member of (10) have the same sign as the corresponding terms in the left-hand member, we shall then examine their relative magnitudes, with the aid of Eq. (17). Unlike the signs, the magnitudes of corresponding terms will be found to disagree.

Before making any detailed calculations, let us observe that we should be able to restrict ourselves to N processes. For if $n_{\mathbf{q}} < N_{\mathbf{q}}^0$, which appears reasonable, and if we assume a Debye frequency distribution, then the

contribution of phonons with frequencies between ν and $\nu + d\nu$ in Eq. (10) is proportional to a factor less than $\nu^2 \exp(-h\nu/kT)$. For U processes, ν is large, and so this term should be small if T is less than the Debye temperature. To the extent to which this reasoning is valid, it substantiates Callaway's assumption that the term $\tau_N^{-1}(N_{\mathbf{q}}^0(\lambda) - N_{\mathbf{q}}^0)$ in Eq. (7) really represents an effect of N processes only.

Given that we are dealing only with N processes, we have conservation of both energy and momentum. Thus, given \mathbf{q}, \mathbf{q}' such that the first term in Eq. (12) does not vanish, we have

$$\omega_{\mathbf{q}} - \omega_{\mathbf{q}'} + \omega_{\mathbf{q}^*} = 0, \quad (20a)$$

$$\mathbf{q} - \mathbf{q}' + \mathbf{q}^* = 0. \quad (20b)$$

The vectors \mathbf{q}' for which Eqs. (20) hold, lie on one of three two-dimensional surfaces in \mathbf{q} space, each of these surfaces corresponding to a different choice of the phonon polarizations.

Since the \mathbf{q}' vectors in the right-hand member of Eq. (10) are restricted to a small number of surfaces, it is obvious that Eq. (10) cannot hold for an arbitrary non-equilibrium state. For in the left-hand member, the vectors \mathbf{q}' range over the entire Brillouin zone. Thus, the validity of Eq. (10) for any nonsteady state depends on our establishing a correspondence between many terms on the left and a much smaller group of terms on the right.

In determining whether or not such a correspondence can be established, let us suppose \mathbf{q}, \mathbf{q}' are chosen such that Eqs. (20) hold. In this case $S_{\mathbf{q}\mathbf{q}'} > 0$ by Eq. (18), and so $\mathbf{q} \cdot \mathbf{q}' > 0$ if the terms corresponding to the same vectors \mathbf{q}, \mathbf{q}' in the left- and right-hand members of (10) are to have the same sign.

By the cosine law, if θ is the angle between \mathbf{q} and \mathbf{q}' ,

$$\cos\theta = (2qq')^{-1}(q^2 + q'^2 - q^{*2}).$$

From the energy conservation condition (20a),

$$q^* = c^{*-1}(c'q' - cq),$$

where $c' \equiv c(\mathbf{q}')$. By the triangle inequality

$$c' > c \quad \text{or} \quad c' > c^*,$$

i.e., \mathbf{q}' is longitudinal. Let us suppose \mathbf{q}' longitudinal, \mathbf{q}^* transverse, and set $c' = c = 2c^*$ (a reasonable assumption for the transverse velocity), $q' = nq$. The cosine law written above now becomes

$$\cos\theta = (2n)^{-1}[8n - 3(n^2 + 1)].$$

We have $n \geq 1$ since $q^* > 0$, and $|\cos\theta| \leq 1$ for $1 \leq n \leq 3$. This determines the range of possible absolute values of \mathbf{q}' contributing to the first term in Eq. (12). We have $\cos\theta > 0$ for $n < 2.215$, i.e., for 0.61 of the possible range.

Two other cases arise, according as $c' = c^* = 2c$ or $c' = 2c = 2c^*$ (different choices of the polarizations). Furthermore, since there are three terms in the right-hand member of Eq. (12), with three cases for each

TABLE I. Percentage of the range of possible values of $n=q'/q$ (labelled "percent agreement") for which $\text{sgn}[S_{\mathbf{q}\mathbf{q}'}]=\text{sgn}(\mathbf{q}\cdot\mathbf{q}')$. The group number corresponds to the first, second, or third term in Eq. (12), and the values $\min n$, $\max n$ delimit the range of n .

Group	c/c^*	c'/c^*	$\min n$	$\max n$	$\text{sgn } S_{\mathbf{q}\mathbf{q}'}$	Percent agreement
1	2	2	1	3	+	61
1	$\frac{1}{2}$	1	$\frac{3}{4}$	∞	+	100
1	1	2	$\frac{1}{2}$	2	+	50
2	$\frac{1}{2}$	1	$\frac{1}{4}$	∞	-	~ 0
2	1	$\frac{1}{2}$	0	4	-	67
2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$	3	-	100
3	2	2	$\frac{1}{3}$	1	+	82
3	1	$\frac{1}{2}$	0	$\frac{5}{4}$	+	100
3	2	1	$\frac{1}{2}$	$\frac{3}{2}$	+	75

term, there are nine distinct sets of \mathbf{q}' vectors to be considered with respect to the sign of $\cos\theta$. The results of the investigation are listed in Table I. These are divided into three groups, corresponding respectively to the three terms in Eq. (12). The min and max values of n delimit the range of values q'/q for which $|\cos\theta| \leq 1$, $q^* > 0$, and the last column of the table gives the percentage of this range for which $\cos\theta$ has the same sign as $S_{\mathbf{q}\mathbf{q}'}$. The sign of the latter is given in the next-to-last column.

The principal contribution to the thermal conductivity comes from longitudinal phonons, since [cf. Ref. 1, Eq. (3.30)] the contribution of a given phonon is proportional to c^2 . For \mathbf{q} longitudinal, the minimum percentage agreement listed in Table I is 61%, thus assuring that the signs of most of the corresponding terms agree in Eq. (10). The worst agreement in Table I, denoted by " ~ 0 " in the fourth row, represents agreement over an interval $\Delta n = \frac{1}{2}$ in an infinite range. In this case \mathbf{q} is transverse.

However, as we have mentioned, the agreement observed between the signs does not extend to the magnitudes of these terms. Thus, in the set of \mathbf{q}' vectors listed in the top row of Table I, $\cos\theta = 1$ for $n = 1$, corresponding to $\mathbf{q}, \mathbf{q}', \mathbf{q}^*$ all collinear. Since \mathbf{q} and \mathbf{q}' are longitudinal in this case and \mathbf{q}^* transverse, the polarization $\mathbf{e}(\mathbf{q}^*)$ is perpendicular to all the other vectors into which it is dotted in Eq. (17), and, thus $S_{\mathbf{q}\mathbf{q}'} = 0$. Therefore, within this group of \mathbf{q}' vectors, the largest term in the left-hand member of (10) corresponds to zero in the right-hand member. This result is in agreement with the fact that A^\dagger , as mentioned in the preceding section, has no diagonal terms; for if \mathbf{q}, \mathbf{q}' are collinear and of the same magnitude and polarization, then either $\mathcal{D}(\mathbf{q}, \mathbf{q}')$ vanishes or, from Table I, $\mathbf{q} \cdot \mathbf{q}' < 0$.

Evidently, the Callaway equation cannot approximate the master equation if the deviations $n_{\mathbf{q}}$ are allowed to vary independently. If, however, we consider the immediate neighborhood of the steady state, it might not be a poor approximation to replace all $n_{\mathbf{q}}$ in Eq. (10), for vectors \mathbf{q} occupying a small solid angle about the direction of ∇T , by their average values and set $n_{\mathbf{q}} = 0$ for \mathbf{q} outside this solid angle. One could then

integrate over the angles in (10), obtain separate values of τ_N^{-1} for each of groups 1, 2, and 3 in Table I, and then average the results. In doing this, one would have to sum over the same two-dimensional surfaces in the left-hand member of (10) as in the right-hand member, and then multiply by a correction factor proportional to the volume of the Brillouin zone included within the solid angle. This would establish the many-to-one correspondence in which all wave vectors in the left-hand sum in (10), lying within the small solid angle about ∇T , would correspond to those wave vectors in the right-hand sum which lie on the two-dimensional surface.

Qualitatively, it would appear from all these considerations, that the Callaway equation should hold approximately near the steady state. For purposes of using the equation to calculate thermal conductivity, it is sufficient that it should hold in the steady state itself, whatever may be its validity for describing the approach to that state. Consequently, in the following section, efforts will be limited to determining τ_N so that the steady-state solution to the Callaway equation satisfies Eq. (10).

5. q DEPENDENCE OF RELAXATION TIMES

The steady-state solution to the Callaway master equation (2) has the form [Ref. 1 Eq. (3.17)]

$$n_{\mathbf{q}} = -\tau_c [1 + (\beta/\tau_N)] \mathbf{C}_{\mathbf{q}} \cdot \nabla T [N_{\mathbf{q}}^0 (N_{\mathbf{q}}^0 + 1)], \quad (21)$$

where β is a constant, independent of \mathbf{q} . If Eq. (10) holds when this solution is substituted into it, then the Callaway equation, for these values of $n_{\mathbf{q}}$, will be identical with the master equation. Therefore, Eq. (21) represents a steady-state solution of the master equation provided τ_N can be so determined that Eq. (21) also satisfies Eq. (10).

When (21) is substituted into (10) and Eq. (18) is used to evaluate $S_{\mathbf{q}\mathbf{q}'}$, the result is

$$\begin{aligned} 1/\tau_N = & q \left[\sum_{\mathbf{q}'} q'^2 \tau_N^{-1}(\mathbf{q}') N_{\mathbf{q}'}^0 (N_{\mathbf{q}'}^0 + 1) \right] \\ & \times \sum_{\mathbf{q}} [\pm \mathcal{D}_{\mathbf{q}\mathbf{q}'} q'^2] c_{\mathbf{q}\mathbf{q}'} n' \cdot \tau(\mathbf{q}') N_{\mathbf{q}'}^0 (N_{\mathbf{q}'}^0 + 1) / \\ & \{ 3 \sum_{\mathbf{q}} q' \tau_N^{-1}(\mathbf{q}') [ll' + mm' + nn'] \\ & \cdot c_{\mathbf{q}\mathbf{q}'} n' \tau(\mathbf{q}') N_{\mathbf{q}'}^0 (N_{\mathbf{q}'}^0 + 1) \}, \quad (22) \end{aligned}$$

where $\tau \equiv \tau_c [1 + (\beta/\tau_N)] \cong \tau_c$, since β/τ_N is ordinarily a small correction. l, m, n are, respectively, the x, y , and z direction cosines of \mathbf{q} , the primes denoting corresponding cosines for \mathbf{q}' . The z axis has been taken to coincide with the direction of ∇T .

Examination of Eq. (22) shows that τ_N is a function of the direction cosines l, m, n of \mathbf{q} . Since the contribution of \mathbf{q} to the thermal conductivity [Ref. 1, Eq. (3.30)] is proportional to n^2 , we are mainly interested in τ_N for \mathbf{q} collinear with ∇T , i.e., $l = m = 0, |n| = 1$. Under these conditions, τ_N is independent of the sign of n . This is seen by an examination of Eqs. (20), and corresponding equations for the other two groups of terms listed in

Table I, which readily shows that reversing the direction of \mathbf{q} has the effect of reflecting all the points \mathbf{q}' , over which the sum $\sum_{\mathbf{q}'} S_{\mathbf{q}\mathbf{q}'}$ is taken in Eq. (10), through the origin in \mathbf{q} space. This means that we merely replace n' by $-n'$ in the numerator of (22) when we replace n by $-n$ ($|n|=1$) in the denominator. The sign and magnitude of the entire expression remain unchanged.

If we set $l=m=0$, $n=1$ in (22), then $\tau_N > 0$, since n' is squared in the denominator, while Table I assures that for most values of n' , $\text{sgn}(\pm \mathfrak{D}_{\mathbf{q}\mathbf{q}'}) = \text{sgn } n'$. Furthermore, if \mathbf{q} is longitudinal, we expect

$$1/\tau_N = AT^3q, \quad (23)$$

where A is constant. This follows from the arguments of Herring⁵ who suggests that for longitudinal \mathbf{q} the surface defined by Eqs. (20) does not collapse as $q \rightarrow 0$, provided crystal anisotropy is taken into account. If Herring's conclusion is correct, then as $q \rightarrow 0$, $\tau_N \propto q$ by Eq. (22). Alternatively, we can argue that if the isotropic approximation, together with Eq. (19), is valid, then $\mathfrak{D}(\mathbf{q}, \mathbf{q}')$ is a function of q'/q . From Table I, q'/q ranges always over the same values, whatever the magnitude of q . Furthermore, if it is true, as Callaway assumes² that $\tau(\mathbf{q}') \propto (q')^{-2}$ in first approximation, q' will cancel out of the surface sum in (22) if the number of points in a surface element is proportional to q'^2 . Thus, the factor multiplying q in (22) will be independent of q , in linear approximation.

This conclusion, however, depends on Herring's argument that τ is proportional to q^{-2} . Since Callaway² has accepted the correctness of Herring's conclusions, this acceptance will be continued tentatively here. Otherwise τ_N^{-1} might depend on a negative power of q , and we should have great difficulty in making any predictions about it.

The index s , determining the temperature dependence of τ_N , can be estimated by substituting (23) into (22) and assuming the Herring result⁵

$$1/\tau_c = BT^3q^2 \quad (24)$$

for longitudinal \mathbf{q} in a cubic crystal. This expression can readily be shown to follow from Eq. (13) by reasoning similar to that by which one obtains Eq. (23) from Eq. (22). In estimating the sums in (22), one might assume a Debye frequency distribution for those sums taken over the entire Brillouin zone. The T dependence of the sum over the two-dimensional surface comes from the factors $N_{\mathbf{q}'}^0(N_{\mathbf{q}'}^0+1)$ which are proportional to T^2 in first approximation, as well as from the factors τ and \mathfrak{D} . With these approximations, putting (23) into (22) and using (24) yields a relation between A and B , plus the identity

$$T^s = T^4. \quad (25)$$

Equations (23) and (25) indicate that if $\tau_c^{-1} \propto q^2$, then $\tau_N \propto q$, in contradiction to the assumption of Callaway²

⁵ C. Herring, Phys. Rev. **95**, 955 (1954).

who identified τ_N^{-1} with the N -process contributions to τ_c^{-1} , thus assuming $\tau_N^{-1} \propto q^2$. The present result, according to Eq. (8), implies that

$$1/\tau_r = BT^3q^2 - AT^4q, \quad (26)$$

so that τ_r becomes negative as $q \rightarrow 0$. However, since it is only phonons with large q which relax by U processes, a negative relaxation time as $q \rightarrow 0$ has no physical significance. The significant relaxation time for small q is τ_c , which is always > 0 .

6. BOUNDARY AND DEFECT SCATTERING

Up to this point, only the contributions of N and U processes have been considered in evaluating the transition matrix in Eq. (1). But for temperatures less than the Debye temperature, U processes are negligible. Consequently, before Eq. (2) can be applied to data taken on finite, imperfect crystals, we must add the effects of phonon scattering by point defects and crystal boundaries.

Boundary scattering [Ref. 1, Sec. VII] can be treated by adding more drift terms to Eq. (1) and then averaging the equation over a cross section of the sample normal to ∇T . The averaged values of $n_{\mathbf{q}}$ obey Eq. (1), with an additional relaxation term $-\tau_b^{-1} = -c/L$ [Ref. 1, Eq. (7.19)] appearing in the diagonal elements of $A_{\mathbf{q}\mathbf{q}'}$ (L is a length of the order of the diameter of the sample). The only effect this term produces in Eq. (7) is to replace τ_c^{-1} by $\tau_c^{-1} + \tau_b^{-1}$.

To discuss bulk-scattering mechanisms, such as impurity atoms, we shall make the assumption that they scatter independently. The transition matrix $A_{\mathbf{q}\mathbf{q}'}$ is then a linear sum of matrices, one for each mechanism. These will give rise to a linear sum of matrices $S_{\mathbf{q}\mathbf{q}'}$ in Eq. (10), each of which will make an additive contribution to τ_N^{-1} .

Two types of point defect will be considered here—an oversized impurity atom or vacancy producing a spherical strain field, and a mass defect. In the case of the first of these, the matrix $A_{\mathbf{q}\mathbf{q}'}$ is calculated very much as in Eq. (12) with the following differences [cf., Ref. 1, Eqs. (4.5), (4.13), (4.38)]:

(1) There are no factors $N_{\mathbf{q}'}^0$ multiplying the D matrices.

(2) For small \mathbf{q}, \mathbf{q}' , the polarization $\mathbf{e}(\mathbf{q}^*)$ in the Φ matrix [Eq. (16)] is replaced by a constant multiplying $|\mathbf{q}' - \mathbf{q}|^{-2}(\mathbf{q}' - \mathbf{q})$ [Ref. 1, Eqs. (4.9) and (4.38)].

(3) The vectors \mathbf{q}' are summed over the surfaces $\omega_{\mathbf{q}'} = \omega_{\mathbf{q}}$. Application of the isotropic acoustic approximation to $\omega_{\mathbf{q}'} = \omega_{\mathbf{q}}$ yields $q' \propto q$. Then we find $S_{\mathbf{q}\mathbf{q}'} \propto q^2 q'^2$ as before. In the surface sum appearing in Eq. (22), since the vectors \mathbf{q}' are summed over a sphere, one can simply multiply the summand by q'^2 and integrate over the angles. Under these circumstances, the q' factors in the sum cancel out, leaving the defect contribution to τ_N^{-1} proportional to q as in the case of N processes. The final result is that we add to the term AT^4q a defect

contribution $A_\delta T^3 q$, where A_δ is proportional to the square of the dilational strain.

Beside this contribution to τ_N^{-1} , a spherical strain field due to an oversized impurity will also contribute a term $B_\delta q^4$ to $1/\tau_c$ [Ref. 1, Eq. (4.39)]. This second result, along with the additive contribution τ_b^{-1} for boundary scattering, is in complete accord with Callaway's assumptions [Ref. 2, Eq. (18)]. However, he makes no provision for a defect contribution to τ_N . The negligibility of A depends on the size of the dilation, and while one may neglect it for isotopy defects, it is probably wrong to do so for impurities in general.

The second type of point defect to be considered here is the mass defect, in which the mass difference between an impurity atom and its neighbors perturbs the kinetic-energy term in the Hamiltonian. This defect contributes a term proportional to ω_q^2 to $A_{qq'}$, and thus a term proportional to ω_q^4/T^2 to $S_{qq'}$ [Ref. 1, Eq. (5.9)]. The surfaces over which \mathbf{q}' is summed are still given by $\omega_q = \omega_{q'}$, and so from Eq. (22) we find, as in the case of the spherical strain field, that the contribution to τ_N^{-1} is of the form $A_\mu T^3 q$. Also, the contribution to τ_c^{-1} for $q \rightarrow 0$ is, assuming a Debye frequency distribution, of the form $B_\mu q^4$ [Ref. 1, Eq. (5.14)].

The mass defect will also contribute to second-order processes in which a three-phonon interaction is associated with scattering by an isotopic impurity. Since the q and T contributions of such processes to $A_{qq'}$ are similar to those for N and U processes,⁶ these second-order effects merely add constants proportional to B_μ to the three-phonon coefficients A and B . Therefore, in fitting experimental data by adjusting A and B , we can merely assume that the second-order processes are included unless it is desired to discuss explicitly the isotopic dependence of these constants.

All of the foregoing results are summarized by the following equations:

$$\begin{aligned} 1/\tau_N &= [AT^4 + (A_\mu + A_\delta)T^3]q, \\ 1/\tau_c &= BT^3q^2 + (B_\delta + B_\mu)q^4. \end{aligned} \quad (27)$$

7. DISCUSSION

While the foregoing sections substantiate Callaway's Eq. (2) as an approximation to the Peierls master equation for states very near the steady state, nevertheless Eq. (27) is in complete disagreement with Callaway's identification of τ_N . Intuitively, it would seem reasonable to assume with Callaway that τ_N^{-1} is the N -process contribution to τ_c^{-1} calculated by Herring,⁵ yet it is

⁶ P. Carruthers, Phys. Rev. **126**, 1448 (1962).

evident that τ_N , in fact, should have a completely different q and T dependence from τ_c .

This conclusion does not in any way conflict with the ostensibly impressive experimental verification of Eq. (2). The N -process correction in Callaway's theory is generally very small, and, in most cases, can be neglected except near the conductivity maximum. In the latter region, Callaway's fit² to the data of Geballe and Hull for Ge exhibits a small discrepancy, which might be attributed to neglect of the τ_N correction.

A real test of the Callaway correction can be made only in the few cases where it is important. In those cases, the discrepancy near the maximum is not removed unless one renounces any attempt to calculate B_μ from the theory of Klemens⁷ and treats this constant as an adjustable parameter. Thus, in alloys of Ge and Si, Toxen found⁸ that the Callaway theory comes out too high near the maximum unless B_μ is treated as adjustable. It is possible, as suggested by Pohl,⁹ that neglect of strain field scattering is responsible for discrepancies encountered in fitting the data in alloys, though such strains should be less important in a mixture of He isotopes, where the τ_N correction is important, and where similar discrepancies were found. For a He-isotope mixture, Callaway suggests¹⁰ that B_μ should be up to several times the value calculated according to Klemens.

Consequently, while the τ_N correction in the form given by Callaway may be a good approximation in a few cases, such as Ge, there is still room for improvement which could be effected by a modified expression for τ_N . Equation (27) gives only the first approximation, and thus it will not hold, in general, above the conductivity maximum. In the higher temperature range, one might add to τ_N^{-1} a term proportional to q^3 which would become dominant as T increases. If the coefficients of all these extra terms are treated as adjustable, one should obtain a good fit while keeping the theoretical expression for B_μ [Ref. 1, Eq. (5.14)].

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⁷ P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955); Ref. 1, Eqs. (5.13), (5.14).

⁸ A. M. Toxen, Phys. Rev. **122**, 450 (1961).

⁹ R. O. Pohl, Phys. Rev. **118**, 1499 (1960).

¹⁰ J. Callaway, Phys. Rev. **122**, 787 (1961).