Attenuating Wave Analysis of Heat Flow in Crystal Lattices*†

Leonard M. Magid

Massachusetts Institute of Technology, Cambridge, Massachusetts

A direct approach to the detailed analysis of the thermal relaxation and conduction processes in crystal lattices in the classical-temperature range is presented in terms of the mechanical energy transported by attenuating lattice waves. A second-order classical perturbation procedure, formulated in terms of time- and space-dependent normal coordinates, is used to solve for the dynamics of a slightly imperfect, nonlinear general crystal lattice model under the influence of an applied temperature gradient. Only the use of a random-phase assumption for initial wave amplitudes at $t=0$ and statistical averaging of the subsequent dynamical response are required for the direct determination of the accepted lattice relaxation times from the time dependence of the stored mechanical-energy density (for first- and second-order perturbation terms). In addition, the well-known anharmonic, mass-fluctuation, and force-fluctuation components of the high-temperature thermal conductivity are found directly from the steady-state mechanical-power density within the lattice. No use is made of the Boltzmann transport equation or standard phonon scattering theory, although the results obtained are wholly consistent with their use. Finally, a brief discussion is given on the extension of this attenuating-wave technique to the corresponding quantum treatment of low-temperature heat flow in crystal lattices.

I. INTRODUCTION

ALTHOUGH several workers have presented accounts of the heat flow within crystal lattices,[1-3] previous studies have been somewhat overly restrictive in their approach. Peierls, in his classic paper on heat conduction in 1929, was able to obtain the quantitative thermal behavior of an uniform temperature lattice directly from the system kinetics. Using a wave-packet approach for the analysis of a nonuniform temperature crystal, however, he was only successful in obtaining the proper qualitative behavior of the lattice thermal conductivity. Others since have refined the wave-packet or phonon-scattering analysis to obtain the correct quantitative thermal-conduction relations, but at the expense of several implicit assumptions; e.g., (1) that the heat flows with the group velocity in a nonlinear, imperfect lattice; (2) that a lattice relaxation time exists; and finally, (3) that the Boltzmann transport equation is applicable to the lattice system.

The analysis presented here eliminates the need for these restrictive assumptions by using a set of attenuating lattice wave (hereafter simply ALW) perturbation solutions that are capable of describing in detail the expected thermal relaxation and conduction properties within a crystal, directly from the average system dynamics.

The ALW perturbation theory is a natural extension of the time-dependent normal mode perturbation theory used by Peierls to determine the average kinetic

response of a uniform temperature lattice.[1] To obtain the corresponding direct evaluation of the average dynamical behavior of a nonuniform temperature system, one need only allow for the simultaneous dependence of the normal coordinates (i.e., traveling wave amplitudes) on both position and time. The resulting time-dependent, spatially-attenuating wave solutions are then capable of describing in detail the expected continuous redistribution in the lattice mode energies as the stationary steady-state conditions develop within a crystal in the presence of a temperature gradient (for first- and second-order perturbation terms).

This analysis is based upon the usual classical model of a completely general 3-dimensional, anisotropic, anharmonic (i.e., up to second order in nonlinearity) crystal inclusive of a light doping of arbitrary substitutional atomic impurities. No restrictions are placed upon the number of atoms per unit cell nor on the range of atomic coupling. The vibrating atoms are treated as simple mass points, while the electronic contributions not of interest here are set aside.

Although classical mechanics is used to simplify the analysis, similar results should be obtainable for the quantized case by simply treating the dynamic variables as quantum operators, and observing the necessary commutation properties. A brief discussion of the anticipated results of such a treatment is given. The full quantum analysis, now near completion, will be published separately.

II. LATTICE DYNAMICS—CLASSICAL PERTURBATION PROCEDURE

The dynamical analysis of the vibration of a completely general nonperiodic and anharmonic crystal containing many atoms per cell and involving arbitrarily long-range atomic couplings would be rather difficult to carry out, if indeed possible. Suitable

[1] R. E. Peierls, Ann. Physik **5**, 3, 1055 (1929).
[2] P. G. Klemens, Solid-State Phys. **7**, 1 (1958).
[3] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960).

approximate solutions can be found, however, if we restrict our scope to the physically reasonable limitations of a slightly imperfect lattice, as defined by the following conditions:

(1) The lattice system of interest has only a light doping of substitutional atomic impurities, randomly distributed in an otherwise completely general perfectly periodic structure.

(2) The temperature at any point within the crystal is enough above the Debye temperature to insure the validity of a classical analysis, yet sufficiently below the melting point of the solid to keep the anharmonic force contributions small.

Within the limitations above, a classical perturbation procedure will be established that proves to be capable

of accounting for the expected nonlinear, mass-fluctuation, and force-fluctuation lattice scattering, relaxation, and thermal conduction effects directly in terms of ALW solutions.

The basic classical equation of motion for the displacement from equilibrium $\mathbf{u}(i,n)$ of the ith atom in the nth unit cell is simply Newton's law in the form

$$M(i,n)\frac{d^2\mathbf{u}(i,n)}{dt^2}=\mathbf{F}(i,n)\,,\qquad(1)$$

where $M(i,n)$ and $\mathbf{F}(i,n)$ are, respectively, the net mass of, and force acting on, atom (i,n). For a slightly imperfect, anharmonic crystal, we shall take $\mathbf{F}(i,n)$ (up to second-order anharmonic contributions only) to be

$$\mathbf{F}(i,n)=-\sum_{j,p}\mathbf{V}(ij,n)\cdot\mathbf{u}(j,p)-\tfrac{1}{2}\sum_{j,p}\sum_{h,q}\mathbf{V}'(ijh,n):\mathbf{u}(j,p)\mathbf{u}(h,q)-\tfrac{1}{6}\sum_{j,p}\sum_{h,q}\sum_{c,w}\mathbf{V}''(ijhc,n):\cdot\mathbf{u}(j,p)\mathbf{u}(h,q)\mathbf{u}(c,w)\,,\quad(2)$$

where the indices i, j, h, and c refer to atoms within a unit cell, while the indices n, p, q, and w range over all of the unit cells within the crystal (unless otherwise specified).

To account for the presence of substitutional atomic impurities at various sites within the crystal, both the atomic masses and the coupling-force constants are permitted here to be dependent upon the unit-cell locations [e.g., $M(i,n)$, $\mathbf{V}(ij,n)$, $\mathbf{V}'(ijh,n)$, etc.].

A classical perturbation procedure patterned after that used by Peierls[1] may readily be established by bringing the basic nonlinear equations of motion [i.e., Eq. (1)] into a form that differs only slightly from the linear equations of a perfectly periodic harmonic lattice of the form

$$m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}=-\sum_{j,p}\mathbf{V}(ij)\cdot\mathbf{u}(j,p)\,,\qquad(3)$$

where m_i and $\mathbf{V}(ij)$ are the mass and force-constant values of an unperturbed system suitably representative of the average behavior of the actual system.

Equation (1), however, may easily be brought by algebraic manipulation into two apparently different (but actually equivalent) perturbation forms in terms

of Eq. (3), as given in Eqs. (4a) and (4b) below.

$$m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}=\mathbf{F}(i,n)+\left[1-\frac{M(i,n)}{m_i}\right]m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}\,,\qquad(4a)$$

or

$$m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}=\mathbf{F}(i,n)+\left[\frac{m_i}{M(i,n)}-1\right]\mathbf{F}(i,n)\,.\qquad(4b)$$

The fact that Eqs. (4a) and (4b) are indeed equivalent can be seen by substituting for $d^2\mathbf{u}(i,n)/dt^2$ from Eq. (1) into the right-hand side of Eq. (4a). Both Eqs. (4a) and (4b) then take the useful form[4]

$$m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}=\mathbf{F}(i,n)+[m_i-M(i,n)]$$
$$\times[M(i,n)]^{-1}\mathbf{F}(i,n)\,.\qquad(4c)$$

Accordingly, by expanding the force constants of Eq. (2) into the average values of Eq. (3) and their corresponding deviation terms [cf. Eq. (6) below] (and introducing the symbol μ to serve as an indicator of the order of perturbation), one arrives at the following classical perturbation equation of motion. (Terms up to second order in μ only are shown.)

$$m_i\frac{d^2\mathbf{u}(i,n)}{dt^2}=-\sum_{j,p}\mathbf{V}(ij)\cdot\mathbf{u}(j,p)-\mu\left\{\sum_{j,p}\left[\left[\frac{m_i}{M(i,n)}-1\right]\mathbf{V}(ij)+\mathbf{W}(ij,n)\right]\cdot\mathbf{u}(j,p)+\tfrac{1}{2}\sum_{j,p}\sum_{h,q}\mathbf{V}'(ijh):\mathbf{u}(j,p)\mathbf{u}(h,q)\right\}$$

$$-\mu^2\left\{\sum_{j,p}\left[\frac{m_i}{M(i,n)}-1\right]\mathbf{W}(ij,n)\cdot\mathbf{u}(j,p)+\tfrac{1}{2}\sum_{j,p}\sum_{h,q}\left[\left[\frac{m_i}{M(i,n)}-1\right]\mathbf{V}'(ijh)+\mathbf{W}'(ijh,n)\right]:\mathbf{u}(j,p)\mathbf{u}(h,q)\right.$$

$$\left.+\tfrac{1}{6}\sum_{j,p}\sum_{h,q}\sum_{c,w}\mathbf{V}''(ijhc):\cdot\mathbf{u}(j,p)\mathbf{u}(h,q)\mathbf{u}(c,w)\right\}+\cdots.\quad(5)$$

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[4] This equivalence becomes significant in the detailed treatment of the mass-fluctuation contributions to the thermal conductivity. Further work on this point will be published later.

Here, the coupling force constants of Eq. (2) have been expressed in terms of average and deviation terms as

$$\mathbf{V}(ij,n)=\mathbf{V}(ij)+\mu\mathbf{W}(ij,n)$$
$$\mathbf{V}'(ijh,n)=\mathbf{V}'(ijh)+\mu\mathbf{W}'(ijh,n), \text{ etc.}$$

(6)

III. TIME-DEPENDENT ATTENUATING LATTICE WAVES

A set of perturbation solutions to Eq. (5) that prove to be convenient for describing the detailed lattice wave behavior of a crystal under the influence of an applied temperature gradient take the general form of attenuated traveling waves. Specifically, the atomic displacements from equilibrium are expressed in terms of the usual unperturbed normal mode traveling waves, but with wave amplitudes (i.e., normal coordinates) that are allowed to take on arbitrary (but assumed small) space and time dependence. That is,

$$\mathbf{u}(i,n)=[2Nm_i]^{-1/2}2\,\mathrm{Re}[\sum_{k,s}\mathbf{A}_i(k,s)Q_{k,s}(t,\mathbf{X}_n)$$

$$\times\exp(i(\mathbf{k}\cdot\mathbf{X}_n-\omega_{ks}t))], \quad (7)$$

where ω_{ks}, $\mathbf{k}$, and $\mathbf{A}_i(k,s)$ are, respectively, the radian frequency, wave vector, and polarization vector of the kth mode and sth polarization branch of the unperturbed lattice wave solutions.

For convenience, the space and time dependence of each mode amplitude is assumed separable in the form

$$Q_{ks}(t,\mathbf{X}_n)=Q_{ks}(t)G(\mathbf{X}_n), \quad (8a)$$

where, because of the expected slight spatial variation of the energy within a crystal in the presence of small applied temperature differences, the space dependence is explicitly allowed to vary as a completely general (but assumed slight) function of cell position $\mathbf{X}_n$. That is,

$$G(\mathbf{X}_n)=[1-\mu(\boldsymbol{\alpha}_{k,s}\cdot\mathbf{X}_n)+\mu^2(\mathbf{X}_n\cdot\boldsymbol{\beta}_{k,s}\cdot\mathbf{X}_n)+\cdots]. \quad (8b)$$

The particular values for the expansion coefficients of Eq. (8b) will later be determined by the spatial dependence of the temperature distribution.[5]

Considerable simplification is achieved by noting that the time-dependent amplitudes that are of interest here are the slowly varying functions of time (in comparison to the frequencies ω) that lead to steady-state effects within a crystal over periods of time that are quite long with respect to the periods of wave oscillation. Any solutions that lead to other then gradual changes in the system will disappear in the averaging process. Accordingly, $\ddot{Q}_{ks}(t)$ will be assumed to be negligible in comparison to $\omega\dot{Q}_{ks}(t)$. In addition, each Q_{ks} will be expressed in series form in terms of assumed small time-dependent changes away from its initial amplitude $Q_{ks}^{(0)}$ as

$$Q_{ks}(t)=Q_{ks}^{(0)}+\mu Q_{ks}^{(1)}(t)+\mu^2 Q_{ks}^{(2)}(t)+\cdots, \quad (8c)$$

where

$$Q_{ks}(t=0)=Q_{ks}^{(0)}.$$

By substituting Eqs. (7) and (8) into Eq. (5), applying the well-known orthogonality relations of the unperturbed normal mode solutions,[6] and then equating equal powers of μ on each side of the resulting equation, one obtains a readily solvable iterative set of first-order linear differential equations. These equations provide the desired link between the time variations of the mode amplitudes (i.e., the expected lattice wave scattering) and the nonlinear and impurity-atom effects in a slightly imperfect crystal.

The resulting values of this perturbation procedure are the time-dependent expansion terms for the wave amplitudes [cf. Eq. (8c)] expressed in terms of the set of initial amplitudes $Q_{ks}^{(0)}$ and the spatial coefficients $\boldsymbol{\alpha}_{k,s}$ and $\boldsymbol{\beta}_{k,s}$ of Eq. (8b). To first and second order in μ, they are[7]

$$Q_{ks}^{(1)}(t)=t(\boldsymbol{\alpha}_k\cdot\mathbf{v}_k)Q_k^0+\frac{1}{4i\omega}\sum_{\pm(k's')}E_{-k,k'}Q_{k'}^0 g[(\omega-\omega')t]+\frac{1}{4i\omega}\sum_{\pm(k's')}\sum_{k''s''}B_{-k,k'k''}Q_{k'}^0Q_{k''}^0 g[(\omega-\omega'-\omega'')t],$$

where

$$g[Zt]=(iZ)^{-1}[\exp(iZt)-1], \quad (9)$$

and (in derivative form for compactness),

$$\dot{Q}_{ks}^{(2)}(t)=(\boldsymbol{\alpha}_k\cdot\mathbf{v}_k)Q_k^1(t)+\frac{1}{4i\omega}\sum_{\pm(k's')}E_{-k,k'}Q_{k'}^1\exp[i(\omega-\omega')t]+\frac{1}{4i\omega}\sum_{\pm(k's')}\sum_{k''s''}B_{-k,k',k''}(Q_{k'}^0Q_{k''}^1+Q_{k'}^1Q_{k''}^0)$$

$$\times\exp[i(\omega-\omega'-\omega'')t]+\frac{1}{4\omega}\sum_{\pm(k's')}\sum_{k''s''}Q_{k'}^0Q_{k''}^0\exp[i(\omega-\omega'-\omega'')t]\left[\boldsymbol{\alpha}_{k'}\cdot\frac{\partial}{\partial\mathbf{k}'}+\boldsymbol{\alpha}_{k''}\cdot\frac{\partial}{\partial\mathbf{k}''}\right]B_{-k,k'k''}$$

$$+\frac{1}{4\omega}\sum_{\pm(k's')}Q_{k'}^0\exp[i(\omega-\omega')t]\left[\boldsymbol{\alpha}_{k'}\cdot\frac{\partial}{\partial\mathbf{k}'}\right]E_{-k,k'}-\frac{1}{i\omega}Q_k^0\boldsymbol{\beta}_k:\left(\omega\frac{\partial}{\partial\mathbf{k}}\mathbf{v}_k+\mathbf{v}_k\mathbf{v}_k\right)$$

$$-\frac{1}{4i\omega}\sum_{\pm(k's')}\sum_{k''s''}\sum_{k'''s'''}B_{-k,k',k'',k'''}Q_{k'}^0Q_{k''}^0Q_{k'''}^0\exp[i(\omega-\omega'-\omega''-\omega''')t]. \quad (10)$$

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[5] An alternative (however, less general) way of introducing the spatial dependence into the energy response is to allow the wave vector $\mathbf{k}$ to become complex in the form $\mathbf{k}=\mathbf{k}_0+i\mu\boldsymbol{\alpha}$. The resulting exponential attenuation is seen to be equivalent to Eq. (8b) to first

The terms $B_{-k,k',k''}$ and $B_{-k,k',k'',k'''}$ involving the coupling of three and four modes, respectively, are due to the nonlinear force terms. The terms $E_{-k,k'}$, coupling only two modes, are the combined results of mass fluctuations and force fluctuations as caused by the presence of substitutional impurity atoms. Specifically,[8]

$$B_{-k,k',k''} = [2N]^{-1/2} \sum_i \sum_{j,L} \sum_{h,R} \mathbf{V}'(ijh) \vdots \mathbf{A}_i^*(k)\mathbf{A}_j(k')\mathbf{A}_h(k'')[m_i m_j m_h]^{-1/2}$$

$$\times \exp[i(\mathbf{k}' \cdot \mathbf{X}_L + \mathbf{k}'' \cdot \mathbf{X}_R)]\delta_{(\mathbf{K},\mathbf{k}-\mathbf{k}'-\mathbf{k}'')}, \quad (11a)$$

$$B_{-k,k',k''k'''} = [2N]^{-1} \sum_i \sum_{j,L} \sum_{h,R} \sum_{c,Z} \mathbf{V}''(ijhc) \vdots\vdots \mathbf{A}_i^*(k)\mathbf{A}_j(k')\mathbf{A}_h(k'')\mathbf{A}_c(k''')[m_i m_j m_h m_c]^{-1/2}$$

$$\times \exp[i(\mathbf{k}' \cdot \mathbf{X}_L + \mathbf{k}'' \cdot \mathbf{X}_R + \mathbf{k}''' \cdot \mathbf{X}_Z)]\delta_{(\mathbf{K},\mathbf{k}-\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')}, \quad (11b)$$

and

$$E_{-k,k'} = C_{-k,k'} + D_{-k,k'},$$

where

$$C_{-k,k'} = \omega'^2 N^{-1} \sum_{i,n} \left[\frac{m_i}{M(i,n)} - 1 \right] \mathbf{A}_i^*(k) \cdot \mathbf{A}_i(k') \exp[i\mathbf{X}_n \cdot (\mathbf{k}'-\mathbf{k})], \quad (11c)$$

$$D_{-k,k'} = N^{-1} \sum_{i,n} \sum_{j,L} \mathbf{W}(ij,n) : \mathbf{A}_i^*(k)\mathbf{A}_j(k')[m_i m_j]^{-1/2} \exp[i\mathbf{k}' \cdot \mathbf{X}_L] \exp[i\mathbf{X}_n \cdot (\mathbf{k}'-\mathbf{k})]. \quad (11d)$$

The results obtained above represent only the instantaneous behavior of the lattice system in terms of small perturbative changes away from an arbitrary initial mode-amplitude distribution. The real difficulty of obtaining a physically meaningful stationary average response for the lattice under the influence of a temperature gradient, will be treated in detail in the next section.

IV. OBSERVABLE LATTICE ENERGY

Local Crystal Energy

A necessary requirement for any proposed set of solutions to the lattice vibrational problem is that the steady-state results lead to time average stored energy values that are consistent with the concept of temperature. For crystals in which temperature gradients exist, the energy that becomes significant here is the macroscopic energy associated with an elemental volume ΔV small enough so that the temperature within it is effectively constant, yet large enough microscopically to be thought of as a subsystem capable of reaching steady-state equilibrium consistent with its own local temperature.

The expression for the instantaneous mechanical energy of an elemental volume ΔV within a completely general crystal lattice has been derived in the companion paper[9] (given here only up to second order in anharmonic terms) to be

$$W_{\Delta V} = \frac{1}{2} \sum_{\substack{i,n \\ \Delta V}} M(i,n)\mathbf{v}(i,n) \cdot \mathbf{v}(i,n) + \frac{1}{2} \sum_{\substack{i,n \\ \Delta V}} \sum_{\substack{j,p \\ \text{all}}} \mathbf{V}(ij,n) : \mathbf{u}(i,n)\mathbf{u}(j,p) + \frac{1}{3!} \sum_{\substack{i,n \\ \Delta V}} \sum_{\substack{(j,p \ h,q) \\ \text{all}}} \mathbf{V}'(ijh,n) \vdots \mathbf{u}(i,n)\mathbf{u}(j,p)\mathbf{u}(h,q)$$

$$+ \frac{1}{4!} \sum_{\substack{i,n \\ \Delta V}} \sum_{\substack{(j,p \ h,q \ c,w) \\ \text{all}}} \mathbf{V}''(ijhc,n) \vdots\vdots \mathbf{u}(i,n)\mathbf{u}(j,p)\mathbf{u}(h,q)\mathbf{u}(c,w), \quad (12)$$

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order in μ. Equation (8b), however, allows a more general variation to higher orders in μ. To date, no real justification has been found for restricting the solution to an exponential attenuation.

[6] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1956).

[7] To simplify notation: $Q_{k,s}^{(0)}$, $Q_{k,s}^{(1)}$, etc. are shortened to Q_k^0, Q_k^1, $\cdots$; $\alpha_{k,s}$, $\beta_{k,s}$, $v_{k,s}$, $\omega_{k,s}$, and $\omega_{k',s'}$ have become simply α_k, β_k, v_k, ω, and ω', respectively. Also, a $\pm$ sign has been introduced under the summation signs of Eq. (9) to indicate that the sums involved also include terms like $Q_{-k'}^{0*}$ and $Q_{-k'}^{0*}$ with a change in the sign of ω' and ω''. Ordinarily the sums on (k',s') include both $+k'$ and $-k'$ modes. The $\pm$ sign here means sums in addition to this.

[8] It should be noted that the restriction on each of these terms that the vector sum of the wave vectors of the coupled modes must add to zero or $\mathbf{K}$ (any reciprocal lattice vector) results (as in the standard phonon treatment) from the periodicity of the unperturbed crystal.

[9] L. M. Magid, preceding article, Phys. Rev. **134**, A158 (1964). The elemental volume ΔV is assumed to contain a fixed number of atoms.

where the sums on atoms (i,n) are limited to the volume ΔV, while the other sums are over the entire crystal.

The determination of the observable (or steady-state average) value of local energy is considerably more involved than the mere substitution of the perturbation solutions into Eq. (12), and subsequent averaging. The basic difficulty is that these solutions are accurate over only limited time intervals due to the series expansion technique used. Well-known statistical procedures, however, do allow for the use of these solutions within the range of their validity. Specifically, a given lattice mode can be thought of as taking on a large number (effectively all) of the possible initial conditions and undergoing the corresponding small perturbative responses over an observational time period. Accordingly, we could treat the over-all nonlinear lattice system as composed of a set of many successive short-time interactions occurring within an observational time period, each describable within the limits of perturbation theory, but each starting out with a different set of initial conditions.

A more convenient way of treating this system, however, is to imagine a single ensemble formed at $t=0$ of all possible amplitudes and phases for each mode. The statistical properties of each ensemble (and, accordingly, the average behavior of that mode) will then, in general, vary slowly with time in accordance with the perturbation solutions already derived, until stationary steady-state conditions are established. In the steady state, both the ensemble statistics and the corresponding average responses must, of course, be time-independent.

The Random-Phase Assumption

For the choice of suitable statistics to govern the ensemble of all possible initial amplitudes and phases

for each mode, we shall again follow Peierls and make the random-phase assumption.[10] That is, at $t=0$, all phase angles are assumed to be equally likely for each mode. As a result, the statistical average of $Q_{ks}{}^0$ (and, in fact, all odd products of mode amplitudes) will be zero. The only terms assumed to have nonzero averages are those independent of initial phase angle (e.g., complex conjugate pairs). Also, for the average of the product of four amplitudes, we shall neglect the less frequent case of all four amplitudes being of the same mode in comparison to the product of two independent complex-conjugate pairs. In mathematical form, the random-phase assumption is then

$$\langle Q_k{}^0 \rangle_{\mathrm{av}} = \langle Q_k{}^0 Q_{k'}{}^{,0} Q_{k''}{}^{,0} \rangle_{\mathrm{av}} = 0, \text{ for all } \mathbf{k},\ \mathbf{k}',\ \text{and } \mathbf{k}'', \tag{13a}$$

$$\omega_{ks}{}^2 \langle Q_{ks}{}^0 Q_{k's}{}^{,0*} \rangle_{\mathrm{av}} = \mathscr{E}_{ks}{}^0 \delta_{s,s'} \delta_{(\mathbf{k}-\mathbf{k}',\mathbf{K})}$$

and the four-mode approximation is

$$\langle Q_{ks}{}^{0*} Q_{k's}{}^{,0*} Q_{k''s}{}^{,,0} Q_{k'''s}{}^{,,,0} \rangle_{\mathrm{av}}$$
$$\approx \langle Q_{ks}{}^0 Q_{ks}{}^{0*} \rangle_{\mathrm{av}} \langle Q_{k's}{}^{,0} Q_{k's}{}^{,0*} \rangle_{\mathrm{av}}$$
$$\times \big[\delta_{s,s''} \delta_{(\mathbf{k}-\mathbf{k}'',\mathbf{K})} \delta_{s',s'''} \delta_{(\mathbf{k}'-\mathbf{k}''',\mathbf{K})}$$
$$+ \delta_{s,s'''} \delta_{(\mathbf{k}-\mathbf{k}''',\mathbf{K})} \delta_{s',s''} \delta_{(\mathbf{k}'-\mathbf{k}'',\mathbf{K})} \big], \tag{13b}$$

where the brackets indicate statistical ensemble averages. The $\mathscr{E}_{ks}{}^0$ values are unspecified initial ensemble averages to be determined later from the existing temperature conditions.

V. TIME DEPENDENCE OF THE LOCAL CRYSTAL ENERGY

Until stationary steady-state conditions become established within the lattice, the statistical average of the local energy relation of Eq. (12) (when expressed in terms of the perturbation solutions of Sec. III) is seen to be dependent upon both position and time. Specifically, up to second-order terms in μ, one finds that

where

$$\langle W_{\Delta V}(\mathbf{x},t) \rangle_{\mathrm{av}} = \frac{N_{\Delta V}}{N} \Big\{ \sum_{k,s} \langle \mathscr{E}_{k,s}(t) \rangle_{\mathrm{av}} \big[1 - 2\mu(\boldsymbol{\alpha}_k \cdot \mathbf{x}) + \mu^2(2\beta_k + \alpha_k \alpha_k) : \mathbf{x}^2 \big] + \mu^2(\text{constants}) \Big\}, \tag{14}$$

$$\mathbf{x} = [N_{\Delta V}]^{-1} \sum_{\substack{n \\ \Delta V}} \mathbf{X}_n = \text{average position of } \Delta V,$$

$$\mathbf{x}^2 = [N_{\Delta V}]^{-1} \sum_{\substack{n \\ \Delta V}} \mathbf{X}_n \mathbf{X}_n = \text{mean square position of } \Delta V,$$

$$N_{\Delta V} = \text{number of unit cells within } \Delta V.$$

The sums taken on n are over all of the unit cells within ΔV.

The time dependence of the average local energy of Eq. (14) is seen to be entirely contained in the average mode energy terms $\langle \mathscr{E}_{ks}(t) \rangle_{\mathrm{av}}$, as defined (up to second order in μ but only linear in t) by

$$\langle \mathscr{E}_{k,s}(t) \rangle_{\mathrm{av}} = \omega^2 \langle Q_{ks}(t) Q_{ks}{}^*(t) \rangle_{\mathrm{av}}$$
$$= \mathscr{E}_{ks}{}^0 + t \big[2\mu(\boldsymbol{\alpha}_k \cdot \mathbf{v}_k) \mathscr{E}_{ks}{}^0 - (H_A + H_{\Delta M} + H_{\Delta F}) \big] + \cdots, \tag{15}$$

[10] Peierls (cf. Ref. 1) has shown that a random-phase assumption leads to Maxwell-Boltzmann statistics for a uniform temperature lattice system in the classical temperature range. It seems reasonable to assume that this result will be only slightly modified in the small temperature gradient system.

where $\mathcal{E}_{ks}{}^0=\omega^2\langle Q_k{}^0Q_k{}^{0*}\rangle_{\mathrm{av}}$ is simply the initial value of the average energy of the (k,s) mode. For $t>0$, the net linear time dependence of the average mode energy of Eq. (15) results from the combined effects of mode attenuation (as given in the α_k term) and the nonlinear, mass-fluctuation, and force-fluctuation lattice scattering effects (as represented by the H_A, $H_{\Delta M}$, and $H_{\Delta F}$ terms, respectively), where

$$H_A=\frac{V}{16\pi^2}\sum_{k',s'}\int_{\sigma_{\omega''}}\sum_{s''}\frac{|B_{-k,k',k''}|^2}{\omega\omega'\omega''^2|v_{k''}|^3}[(\omega'\mathcal{E}_k{}^0\mathcal{E}_{k''}{}^0+\omega''\mathcal{E}_k{}^0\mathcal{E}_{k'}{}^0-\omega\mathcal{E}_{k'}{}^0\mathcal{E}_{k''}{}^0)\delta(\omega-\omega'-\omega'')+(-\omega'\mathcal{E}_k{}^0\mathcal{E}_{-k''}{}^0$$

$$-\omega''\mathcal{E}_k{}^0\mathcal{E}_{-k'}{}^0-\omega\mathcal{E}_{-k'}{}^0\mathcal{E}_{-k''}{}^0)\delta(\omega+\omega'+\omega'')+(\omega'\mathcal{E}_k{}^0\mathcal{E}_{-k''}{}^0-\omega''\mathcal{E}_k{}^0\mathcal{E}_{k'}{}^0-\omega\mathcal{E}_{k'}{}^0\mathcal{E}_{-k''}{}^0)\delta(\omega-\omega'+\omega'')$$

$$+(-\omega'\mathcal{E}_k{}^0\mathcal{E}_{k''}{}^0+\omega''\mathcal{E}_k{}^0\mathcal{E}_{-k''}{}^0-\omega\mathcal{E}_{-k''}{}^0\mathcal{E}_{k'}{}^0)\delta(\omega+\omega'-\omega'')]d\sigma_{\omega''}, \quad (16\mathrm{a})$$

$$H_{\Delta M}=\frac{V}{32\pi^2}\int_{\sigma_{\omega'}}\sum_{s'}\frac{|C_{-k,k'}|^2}{\omega\omega'^2|v_{k'}|^3}[(\omega'\mathcal{E}_k{}^0-\omega\mathcal{E}_{k'}{}^0)\delta(\omega-\omega')+(-\omega'\mathcal{E}_k{}^0-\omega\mathcal{E}_{-k'}{}^0)\delta(\omega+\omega')]d\sigma_{\omega'}, \quad (16\mathrm{b})$$

$$H_{\Delta F}=\frac{V}{32\pi^2}\int_{\sigma_{\omega'}}\sum_{s'}\frac{|D_{-k,k'}|^2}{\omega\omega'^2|v_{k'}|^3}[(\omega'\mathcal{E}_k{}^0-\omega\mathcal{E}_{k'}{}^0)\delta(\omega-\omega')+(-\omega'\mathcal{E}_k{}^0-\omega\mathcal{E}_{-k'}{}^0)\delta(\omega+\omega')]d\sigma_{\omega'}. \quad (16\mathrm{c})$$

The integrals above are over constant ω surfaces in $\mathbf{k}$ space that arise from the usual transformation from a discrete sum to integration over all modes.[11]

Relaxation Time Determination

The time dependence of the average local energy of Eqs. (14) and (15) simply indicates that the lattice system will not, in general, be stationary for an arbitrary set of initial mode energies. For the determination of stationary energy distributions consistent with Eqs. (14) and (15), it is convenient to treat the cases of uniform and nonuniform applied temperatures separately. In this regard, it is relatively easy to first establish that for an uniform temperature crystal in thermal equilibrium the well-known classical equipartition distribution is indeed a stationary solution of Eq. (15). The redistribution of energy away from thermal equilibrium following the application of a temperature gradient can then be traced directly in Eqs. (14) and (15) as the system approaches its new stationary steady-state behavior.

A. Uniform Applied Temperature Case

Note first that if we assume an uniform absolute temperature T_0 as our spatial boundary condition, the entire crystal would be homogeneous and all spatial dependence of average energy must vanish. Accordingly, all α_k and $\beta_k=0$. Under such circumstances, the time dependence of the energy per mode [i.e., $\langle\mathcal{E}_{ks}(t)\rangle_{\mathrm{av}}$ for $\alpha_k=0$ and $\beta_k=0$] is seen to vanish if each of the initial-mode values of $\mathcal{E}_{ks}{}^0$ is independent of ω and k. In particular, the lattice system will be time-independent if

$$\mathcal{E}_{ks}{}^0=\kappa T_0, \quad (17)$$

where $\kappa=$ Boltzmann constant. As expected, this is the

well-known classical result for a crystal in steady-state thermal equilibrium. All modes have the same average energy κT_0. This result follows immediately from Eqs. (15) and (16) because of the delta-function dependence on the frequencies.[12]

B. Nonuniform Applied Temperature Case

For the more general case of nonuniform temperatures within the crystal as imposed by the surroundings, α_k and β_k are not necessarily zero. It is convenient to think of this system as starting from uniform temperature thermal equilibrium at T_0 (for $t<0$), and to assume that a small increase be made in temperature along one of the surrounding boundary walls at $t=0$. In this way, a temperature variation is established in a given direction (say along the x axis) with the temperature at the other end (i.e., $x=0$) held at T_0.

During the values of time *immediately* following $t=0$, the values of $\mathcal{E}_{ks}{}^0$ are still κT_0. The statistical average mode energies of Eq. (15), however, are seen to change with time. Up to the linear time dependence given in Eq. (15), one finds that

$$\langle\mathcal{E}_{ks}(t)\rangle_{\mathrm{av}}=\kappa T_0[1+2\mu(\boldsymbol{\alpha}_k\cdot\mathbf{v}_k)t]. \quad (18)$$

The time dependence of Eq. (18) simply confirms the expected result that the nonuniform temperature lattice system will not remain stationary for the uniform temperature distribution. As a result, one must now find a new mode energy distribution for $\mathcal{E}_{ks}{}^0$ that will lead to the time independence of the statistical average energy expression of Eq. (15) with $\alpha_k\neq0$.

But, because of the very slight change in the temperature conditions in this case, it seems reasonable to

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[11] The delta functions of frequency arise from integrals of the form

$$\int_{\omega'=0}^{\omega_{\max}'}\left[\frac{\sin^2[(\omega-\omega')/2]t}{[(\omega-\omega')/2]^2}\right]d\omega'\approx2\pi t\delta(\omega-\omega').$$

[12] In the absence of umklapp processes [as pointed out by P. Carruthers, Rev. Mod. Phys. **33**, 1 (1961)], additional thermal equilibrium solutions of the form

$$\mathcal{E}_{ks}{}^0=\kappa T_0[1+\mu(\mathbf{k}\cdot\mathbf{v}/\omega)]$$

for $\mathbf{v}=$ an arbitrary velocity, constant for all modes would then be possible. That these solutions are also allowed by Eq. (15) when $\mathbf{K}=0$ serves as additional verification of this procedure.

expect that the energy distribution should be only slightly changed. Furthermore, one might expect that while varying in time, the system is actually moving towards its new stationary state. That this is indeed the case can readily be seen by trying as a possible stationary distribution the value attained by $\langle \mathcal{E}_{ks}(t) \rangle_{av}$ in the assumed short time period τ_{ks} [i.e., τ is assumed small enough here so as to warrant the omission of higher order than linear time terms in Eq. (15)]. By using

$$\mathcal{E}_{ks}^{0} = \kappa T_0 [1 + 2\mu(\alpha_k \cdot \mathbf{v}_k)\tau_{ks}] \qquad (19)$$

in Eqs. (15) and (16) as a possible value for $\mathcal{E}_{ks}^{0}$, one finds that the linear time dependence does indeed vanish (to terms up to second order in μ), leaving

$$\langle \mathcal{E}_{ks}(t) \rangle_{av} = \kappa T_0 [1 + 2\mu(\alpha_k \cdot \mathbf{v}_k)\tau_{k,s}] \qquad (20)$$

as the stationary distribution for the nonuniform temperature system.

The result of Eq. (20) is based upon two necessary requirements; first, that

$$(1) \quad \alpha_{k,s} = \alpha_{-k,s}, \qquad (21)$$

and second, that

$$(2) \quad [\tau_{ks}]^{-1} = (\kappa T_0)^{-1} [H_A + H_{\Delta M} + H_{\Delta F}]. \qquad (22)$$

The first restriction, that the linear spatial expansion coefficients be even functions of $\mathbf{k}$, requires physically that both the forward and backward waves be equally attenuated in the same direction in the stationary system [cf. Eqs. (7) and (8)]. This is wholly consistent with having larger atomic displacements at the hotter end of the crystal.

Equation (22), on the other hand, when expressed in terms of Eq. (16) gives the accepted quantitative expressions for the lattice relaxation times τ_{ks} directly, as values necessary for the linear time independence of the lattice energy (up to second order in μ). Specifically, we find that $[\tau_{ks}]^{-1}$ consists of the additive reciprocal contributions from anharmonic, mass-fluctuation, and force-fluctuation effects, respectively, as

$$[\tau_{ks}]^{-1} = [\tau_{ks}]_A^{-1} + [\tau_{ks}]_{\Delta M}^{-1} + [\tau_{ks}]_{\Delta F}^{-1}, \qquad (23)$$

where, for a completely general slightly imperfect and anharmonic lattice

$$[\tau_{ks}]_A^{-1} = \frac{V\kappa T_0}{4\pi^2} \sum_{k',s'} \sum_{s''} \int_{\sigma_{\omega''}} \frac{|B_{-k,k',k''}|^2}{\omega'^2 \omega''^2 |v_{k''}|^3} d\sigma_{\omega''}, \qquad (24a)$$

$$[\tau_{ks}]_{\Delta M}^{-1} = \frac{V}{16\pi^2} \sum_{s'} \int_{\sigma_{\omega'}} \frac{|C_{-k,k'}|^2}{\omega'^2 |v_{k'}|^3} d\sigma_{\omega'}, \qquad (24b)$$

$$[\tau_{ks}]_{\Delta F}^{-1} = \frac{V}{16\pi^2} \sum_{s'} \int_{\sigma_{\omega'}} \frac{|D_{-k,k'}|^2}{\omega'^2 |v_{k'}|^3} d\sigma_{\omega'}. \qquad (24c)$$

The integrals here are taken over surfaces of constant frequency in $\mathbf{k}$ space.

Further agreement with the expected thermal properties of the nonuniform temperature lattice system, along with the determination of α_{ks}, come out of the study of the spatial dependence of average crystal energy to be discussed next.

VI. SPACE DEPENDENCE OF THE LOCAL CRYSTAL ENERGY

Attenuation Coefficient Determination

Up to this point we have not dwelled upon the spatial dependence of the average local energy of Eq. (14). In deriving the stationary energy distribution for the nonuniform temperature crystal in Sec. V, it proved sufficient to consider only the steady-state values of the average mode energies $\langle \mathcal{E}_{ks}(t) \rangle_{av}$. But as can readily be seen from Eq. (14), the $\langle \mathcal{E}_{ks}(t) \rangle_{av}$ terms are effectively the per mode values of the average local energy for only the elemental regions in the $x=0$ plane where the temperature is T_0. That is, from Eq. (14) at $x=0$

$$\langle W_{\Delta V}(x=0) \rangle_{av} = \frac{N_{\Delta V}}{N} \sum_{k,s} \langle \mathcal{E}_{ks}(t) \rangle_{av}$$

$$= \frac{N_{\Delta V}}{N} \kappa T_0 \sum_{k,s} [1 + 2\mu(\alpha_k \cdot \mathbf{v}_k)\tau_{ks}]. \qquad (25)$$

For all other positions $\mathbf{x}$ within the crystal, the stationary average value of the local energy of Eq. (14) in terms of Eq. (20) is seen to be (up to only linear terms in $\mathbf{x}$ and t)

$$\langle W_{\Delta V}(\mathbf{x}) \rangle_{av} = \frac{N_{\Delta V}}{N} \kappa T_0 \sum_{k,s} [1 + 2\mu(\alpha_k \cdot \mathbf{v}_k)\tau_{ks}]$$
$$\times [1 - 2\mu(\alpha_k \cdot \mathbf{x})]. \qquad (26)$$

But if we now make the rather reasonable assumption that the local value of the average mechanical energy at each point within the crystal reaches its steady-state value by the same rule for the shift in distribution as that obtained for $x=0$, we arrive at a consistent definition of the local temperature $T(\mathbf{x})$. From a comparison of Eqs. (25) and (26), one can readily see that the per mode value of the local average energy at position $\mathbf{x}$ of Eq. (26) can be brought into the same form as given in Eq. (25) for $x=0$, e.g.,

$$[\langle W_{\Delta V}(\mathbf{x}) \rangle_{av}]_{k,s} = \frac{N_{\Delta V}}{N} \kappa T(\mathbf{x})[1 + 2\mu(\alpha_k \cdot \mathbf{v}_k)\tau_{ks}], \qquad (27)$$

if one defines the local temperature of the macroscopic elemental volume at position $\mathbf{x}$ to be (to zero and first order in $\mathbf{x}$ only)

$$T(\mathbf{x}) = T_0 [1 - 2\mu(\alpha_k \cdot \mathbf{x})]. \qquad (28)$$

On comparison of Eq. (28) with a Taylor series expansion of the nonuniform temperature distribution

within the crystal about $\mathbf{x}=0$, in the form

$$T(\mathbf{x})=T_0-(\boldsymbol{\nabla}T)_0\cdot\mathbf{x}+\tfrac{1}{2}(\mathbf{x}\cdot\boldsymbol{\nabla}_0)^2T+\cdots, \quad (29)$$

we finally arrive at a determination of the spatial expansion coefficients α_k; that is

$$2\mu\alpha_k=-(\boldsymbol{\nabla}T)_0/T_0. \quad (30)$$

As a result of Eq. (30), the shift in the steady-state energy distribution (per mode) in the presence of small temperature gradients [cf. Eq. (20)] is now seen to be identical to the standard results of the Boltzmann transport equation and the relaxation time assumption in the classical limit.[2] The steady-state average mode energy in the presence of a temperature gradient now takes the familiar form (up to first order in $\mathbf{x}$ and t, but second order in scattering)

$$\langle\mathscr{E}_{ks}(t)\rangle_{\mathrm{av}}=\kappa T_0\left[1-\frac{(\boldsymbol{\nabla}T)_0}{T_0}\cdot\mathbf{v}_k\tau_{ks}\right]. \quad (31)$$

In addition, the steady-state average value of the local energy of an elemental volume ΔV within the crystal is now seen to have the expected linear spatial dependence to the same order of perturbation as Eq.

(31), as given by

$$\langle W_{\Delta V}(\mathbf{x})\rangle_{\mathrm{av}}=\frac{N_{\Delta V}}{N}\frac{T(\mathbf{x})}{T_0}\sum_{k,x}\langle\mathscr{E}_{ks}(t)\rangle_{\mathrm{av}}$$

$$=\frac{N_{\Delta V}}{N}\left[1-\frac{(\boldsymbol{\nabla}T)_0}{T_0}\cdot\mathbf{x}\right]\sum_{k,s}\langle\mathscr{E}_{ks}(t)\rangle_{\mathrm{av}}, \quad (32)$$

where N and $N_{\Delta V}$ are the number of unit cell within ΔV and within the entire crystal, respectively, and $\langle\mathscr{E}_{ks}(t)\rangle_{\mathrm{av}}$ is the average energy per mode as defined by Eq. (31).

VII. EVALUATION OF THE LATTICE THERMAL CONDUCTIVITY

The determination of the lattice component of thermal conductivity can now be made directly from the steady-state statistical average mechanical energy transported within the lattice. The instantaneous mechanical energy flow in a given direction ($+x$, for instance) has already been derived from a general mechanical "Poynting" theorem by the author[9] (shown here to first-order anharmonic terms)

$$S_x=A_x^{-1}\Big[\tfrac{1}{2}\sum_{\substack{i,n\\n_x>0}}\sum_{\substack{j,p\\p_x<0}}\mathbf{V}(ij,n):[\mathbf{u}(i,n)\mathbf{v}(j,p)-\mathbf{u}(j,p)\mathbf{v}(i,n)]$$

$$+\tfrac{1}{3}\sum_{\substack{i,n\\n_x>0}}\sum_{\substack{(j,p\ h,q)\\q_x<0\\p_x<0}}\mathbf{V}'(ijh,n):\cdot[\mathbf{u}(i,n)\mathbf{u}(h,q)\mathbf{v}(j,p)-\mathbf{u}(j,p)\mathbf{u}(h,q)\mathbf{v}(i,n)]$$

$$+\tfrac{1}{3}\sum_{\substack{(i,n\ h,q)\\n_x>0\\q_x>0}}\sum_{\substack{j,p\\p_x<0}}\mathbf{V}'(ijh,n):\cdot[\mathbf{u}(i,n)\mathbf{u}(h,q)\mathbf{v}(j,p)-\mathbf{u}(j,p)\mathbf{u}(h,q)\mathbf{v}(i,n)]+\cdots\Big]. \quad (33)$$

By inserting the attenuating wave solutions of Sec. III, using a counting argument presented in the companion paper mentioned above,[9] and taking the statistical average of the resulting relation, one finds that (up to first order in power flow terms)

$$\langle S_x(t)\rangle_{\mathrm{av}}=V^{-1}\sum_{k,s}\langle\mathscr{E}_{k,s}(t)\rangle_{\mathrm{av}}[v_k]_x. \quad (34)$$

As is expected, the first-order average mechanical power density (i.e., heat flow) per mode does indeed equal the product of the average stored energy density and the group velocity. By using the stationary value of $\langle\mathscr{E}_{ks}(t)\rangle_{\mathrm{av}}$ found in Eq. (31), one then has for the steady-state power flow

$$\langle S_x\rangle_{\mathrm{av}}=\kappa V^{-1}\sum_{k,s}[T_0-(\boldsymbol{\nabla}T\cdot\mathbf{v}_k)\tau_{ks}](v_k)_x, \quad (35)$$

which, because $\mathbf{v}_k=-\mathbf{v}_{-k}$, reduces to

$$\langle S_x\rangle_{\mathrm{av}}=-\kappa V^{-1}\sum_{k,s}(\boldsymbol{\nabla}T\cdot\mathbf{v}_k)\tau_{ks}(v_k)_x. \quad (36)$$

Finally, by determining the other components of the

steady-state average first-order mechanical-power density, one derives the well-known thermal conductivity relation

$$\langle\mathbf{S}\rangle_{\mathrm{av}}=-\mathbf{K}\cdot\boldsymbol{\nabla}T, \quad (37)$$

where the resulting lattice component of the thermal conductivity in the classical temperature range,

$$\mathbf{K}=\kappa V^{-1}\sum_{k,s}\mathbf{v}_k\tau_{ks}\mathbf{v}_k, \quad (38)$$

is seen to be in complete agreement with the results of the standard phonon scattering technique[2] [cf. Eq. (24) for the detailed form of the anharmonic, force-fluctuation, and mass-fluctuation contributions to the relaxation time τ_{ks}].

VIII. QUANTUM FORM OF THE ALW ANALYSIS

The extension of the classical ALW analysis presented here to the corresponding quantum treatment is straightforward in concept, although somewhat involved in execution. One must, of course, treat the classical displacement and momentum variables as

quantum operators having the required commutation properties; but, as is well known, the basic dynamical equations of motion for the quantum operators (using the Heisenberg representation) are identical in form to the classical equations of motion. The dynamical perturbation analysis for the nonlinear response of the classical variables then carries over in substantially the same form (i.e., with care taken to obey commutator properties) to the study of the behavior of the corresponding quantum operators.

In particular, the classical time- and space-dependent traveling wave amplitudes (or normal coordinates) become time- and space-dependent annihilation and creation operators. The energy distribution necessary for thermal equilibrium (in the uniform temperature sample) has already been found to have the expected Bose-Einstein form. Furthermore, the stationary form of the quantum mode energy density in the presence of a temperature gradient seems to agree with the shifted Bose-Einstein expression (as is expected from the Boltzmann transport equation), although this phase of the work has not been completed. The derivation of the low-temperature form of the lattice thermal conductivity should then follow directly from the steady-state average mechanical-power density within the crystal. The full details of the quantum ALW analysis, when completed, will be published separately.

IX. COMPARISON OF ALW ANALYSIS WITH STANDARD PHONON SCATTERING THEORY

Because of the obvious overlap of the classical ALW theory presented here with the standard phonon scattering-Boltzmann transport analysis of heat flow in the classical limit,[2,3] a brief comparison of the two approaches seems to be in order. Both procedures start with the same basic slightly perturbed lattice model, use effectively the same statistics,[10] and both do, indeed, arrive at the same results for the shifted energy distribution, relaxation times, and thermal conductivity from second-order perturbation terms. Furthermore, since the phonon wave-packet concept and the ALW analysis are both based upon linear combinations of the unperturbed normal-mode traveling wave solutions, they are, in principle, equivalent.

In practice, however, when it comes to evaluating the storage and transport of lattice energy within nonuniform temperature systems, the two procedures differ markedly. The basic form of the ALW solutions was chosen so as to allow conveniently for the expected time and space dependence of the average mechanical-energy density within the lattice. As a result, the lattice relaxation time components appear quite naturally as parameters necessary for the linear time independence of the average local mechanical energy when stationary steady-state conditions are established (i.e., up to second order in perturbation). The lattice thermal conductivity is also obtainable in a straightforward

way, directly from the steady-state average mechanical-power density within the crystal. In the standard phonon scattering approach, on the other hand, one must rely upon the circuitous route provided by the application of the Boltzmann transport equation and the two assumptions regarding the existence of a lattice relaxation time and the flow of heat with the group velocity (in a nonlinear system) to obtain the same results.

Finally, the ALW analysis yields a direct evaluation of the predominately linear spatial dependence of the local temperature within the nonuniform-temperature lattice system. Although this result is usually omitted from the standard Boltzmann transport approach, it appears here quite simply from the spatial dependence of the average local energy when evaluated to the same order in perturbation terms as the other well-known heat-flow results (i.e., second order in scattering, but only first order in x and t).

X. CONCLUSIONS

We have shown that the well-known thermal relaxation and conduction properties of slightly imperfect and nonlinear crystal lattices under nonuniform temperature conditions (in the classical temperature range) can indeed be determined directly from the average system dynamics with the application of ALW solutions. By using a set of time-varying and spatially-attenuating lattice modes in a classical perturbation procedure, we were able to derive the accepted anharmonic, mass-fluctuation, and force-fluctuation contributions to both the lattice relaxation times and the resulting thermal conductivity directly from the average mechanical energy transported. No use was made of either the Boltzmann transport equation or the usual assumptions regarding the existence of a lattice relaxation time and the flow of heat with the group velocity. The heat-flow results as derived here are restricted only by the conditions required for the validity of the classical perturbation theory applied, namely[13]:

(1) that the temperatures within the crystal be well below the melting point of the solid, yet above the Debye temperature, (2) that only a light doping of randomly distributed substitutional atomic impurities be present, (3) and that the temperature drop across the sample be much less than the absolute temperatures within (i.e., $\Delta T/T \ll 1$).[14]
With these restrictions, only the use of the random-phase assumption for the statistical description of the ensemble of all possible initial amplitudes and phases

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[13] See Secs. I and II for further details.

[14] The first-order spatial expansion terms of Eqs. (8b) and (30) are seen to be relatively good approximations only if $(\nabla T/T) \cdot \mathbf{X}_n \ll 1$ for all points within the crystal. For $\mathbf{X}_n$ taking its maximum value equal to the crystal length L in the direction of ∇T, then

$$(\nabla T \cdot \mathbf{L})/T_0 \approx \Delta T/T_0 \ll 1$$

serves as one criterion for the validity of the usual linear heat-flow results given here.

(at $t=0$) was found necessary for the evaluation of the expected average lattice behavior from first- and second-order perturbation terms.

Higher order effects can, in principle, be studied directly with the ALW analysis. However, it turns out to be increasingly difficult to determine the relative importance of various errors in the perturbation solutions, the statistics employed, and the other physical effects omitted from the simple atomic model as one attempts to refine the calculations.

Further work on the extension of the ALW analysis to the quantum treatment to eliminate the high-temperature restriction is now near completion and should be published shortly. The application of the attenuating wave technique to other many-body quantum wave-transport mechanisms (e.g., electron conduction) is also under investigation.

Temperature Dependence of Paramagnetic Resonance Lines*†

I. Svare‡ and G. Seidel§

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

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Changes in the position and shape of paramagnetic absorption lines of Nd^{3+} in neodymium ethyl sulfate, Ni^{2+} in nickel fluosilicate, and Cu^{2+} in copper potassium sulfate have been observed at 30 kMc/sec in the temperature range from 0.4 to 4.2°K. The observed shifts are compared to first and second line moments calculated from spin-spin interactions when the average populations of the spin levels are weighted by the proper Boltzmann factors. In this manner it is possible to determine the magnitude and sign of the exchange interaction $\mathcal{H}_{ij} = A\,\mathbf{S}_i \cdot \mathbf{S}_j$ between spins. We find a ferromagnetic interaction $A = -(3.9 \pm 0.4) \times 10^{-18}$ erg between nearest-neighbor Ni^{2+} ions in $NiSiF_6 \cdot 6H_2O$ with no evidence of anisotropic exchange. Nearest-neighbor spins at similar lattice positions in $K_2Cu(SO_4)_2 \cdot 6H_2O$ appear to be coupled by an exchange interaction of approximately $A = -9 \times 10^{-18}$ erg, while the exchange between the two neighboring dissimilar Cu^{2+} ions in the unit cell is $A = -1.4 \times 10^{-18}$ erg. Evidence for a weak anisotropic and antiferromagnetic coupling in $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ is presented. We have observed magnetostatic modes in copper salts at low temperature, and this effect is briefly discussed in relation to the present type of experiment.

I. INTRODUCTION

PARAMAGNETIC resonance lines in solids may be broadened by several effects. (a) The crystal field may vary over the ionic positions in the lattice because of crystal imperfections. (b) The spin-lattice interaction may be sufficiently strong that the lines are lifetime broadened. (c) The spins may interact strongly via dipolar and exchange forces. (d) There may exist unresolved hyperfine interactions.

In a magnetically concentrated salt effect (c) will usually be dominant at low temperature. Van Vleck[1] first calculated the resonance line shape in the presence of weak spin-spin coupling by the method of line moments, and his theory has been used in a number of cases to explain observed line shapes. The strength of the exchange interaction can be deduced from measured line moments since the dipolar part of the coupling is calculable from the dimensions of the crystal lattice and the g values.

The theory given by Van Vleck is a high-temperature approximation, valid when $kT \gg h\nu$, in that the spin levels are all taken to have the same populations. For $kT \leq h\nu$ the populations of the levels have to be weighted by the proper Boltzmann factors, and this may influence the line moments. The temperature dependence of the line moments has been considered by Pryce and Stevens,[2] by Kambe and Usui[3] and in more detail by McMillan and Opechowski.[4] Qualitatively it is easy to

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