Scattering of Neutrons by an Anharmonic Crystal

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The one-phonon differential scattering cross section for the coherent scattering of thermal neutrons by an anharmonic Bravais crystal is obtained correct to the lowest nonvanishing order in the anharmonic force constants. Cubic and quartic anharmonic terms are retained in the crystal's Hamiltonian. It is found that the δ-function peaks in the energy distribution of the scattered neutrons for a fixed momentum transfer (which occur at the unperturbed phonon energies) in the harmonic approximation are broadened and their positions are shifted in an anharmonic crystal. Some numerical results for the magnitudes of the phonon widths and shifts are obtained for a simple model of a face-centered cubic crystal.

I. INTRODUCTION

THE diffraction of neutrons by crystals has been the subject of much experimental and theoretical study since the middle of the nineteen thirties. Like x rays, thermal neutrons have a de Broglie wavelength of the order of the interatomic spacings in crystals so that they can be used in diffraction studies. However, unlike x rays, whose energies are about a million times greater, thermal neutrons have energies which are of the order of the energies of the lattice vibrations. This means that measurements of the energies of neutrons scattered by crystals as functions of the scattering angle can provide information about the energies, and hence the frequencies, of the lattice vibrations with a detail which it is presently impossible to obtain by other means.

The earliest work was primarily concerned with the elastic scattering of neutrons and with the scattering of neutrons by magnetic crystals. Then in 1944, in a fundamental paper, Weinstock[1] derived expressions for the inelastic cross sections for the scattering of a neutron by processes in which the neutron either gains energy from or loses energy to the crystal.

In a crystal whose atoms interact with Hooke's law forces, that is, in a crystal whose potential energy is expanded up to quadratic terms in the displacements of the atoms from their equilibrium positions, the motions of the atoms can be expressed as the superposition of the vibrations of independent harmonic oscillators of which there are as many as there are degrees of freedom in the crystal. Each of these independent modes of vibrations, or normal modes as they are called, has its own characteristic frequency. It is characterized by a wave vector $\mathbf{k}$ whose magnitude is the reciprocal of the wavelength of the lattice wave to which it corresponds, and by an index j which specifies the polarization of the wave. It is well known that a harmonic oscillator of angular frequency $\omega(\mathbf{k}j)$ has an infinity of equally spaced energy levels, the spacing between consecutive levels being $\hbar\omega(\mathbf{k}j)$. This quantum of energy is called a "phonon," a term apparently due to Tamm,[2] and if the oscillator is in its n state of excitation, this situation is described by saying that there are n phonons in the mode $(\mathbf{k}j)$.

In his work, Weinstock calculated the inelastic cross sections only for one-phonon processes, that is, processes in which a neutron either creates or absorbs a single vibrational quantum of energy. Although his work has subsequently been extended to the case of multiphonon processes,[3] the one-phonon processes remain the most interesting from the standpoint of the information they give about the dynamical properties of crystals. With a proper choice of experimental conditions (low temperatures, low incident neutron energies, high nuclear masses) it seems that the multiphonon effects can be made negligible or at least reduced to the size of a manageable correction. Accordingly, we will not discuss multiphonon processes in this paper.

At this point, we must distinguish between the coherent and incoherent scattering of neutrons. Since a crystal is a periodic array of nuclei, a neutron wave scattered by one nucleus can interfere with those scattered by other nuclei. This interferent scattering is called coherent scattering and both elastic and inelastic scattering will give rise to it. It is stronger the more isotopically pure a crystal is and if the nuclei have no spins. On the other hand, if the nuclei can exist in several isotopic states, and/or have a spin, then because, in general, the various isotopes and the spin orientations will be distributed randomly over the lattice sites, the nuclei will tend to scatter independently of one another. This type of scattering is called incoherent, and it is also found in both elastic and inelastic scattering.

Coherent inelastic scattering of thermal neutrons is of particular interest since from a study of the energy change of the scattered neutrons for a given momentum transfer the phonon dispersion curve, the relation between the frequencies of modes of a given polarization and the wave vector $\mathbf{k}$, can be obtained. Incoherent inelastic scattering is also of considerable interest, since the energy distribution of the scattered neutrons is proportional to the frequency spectrum of the crystal.[4]

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[1] R. Weinstock, Phys. Rev. **64**, 1 (1944).
[2] F. Seitz, in *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952), p. 15.
[3] A. Sjölander, Arkiv Fysik **7**, 375 (1954).
[4] G. Placzek and L. van Hove, Phys. Rev. **93**, 1207 (1954).

However, vanadium and hydrogen are the only elements which scatter thermal neutrons primarily incoherently, so that apart from experiments with alloys there is not much scope for experiments of this type at the present time. Consequently, this paper will be devoted to a discussion of the coherent, inelastic scattering of thermal neutrons by one-phonon processes.

If the scattering of neutrons by a Bravais crystal is studied in the harmonic approximation, the one-phonon scattering cross section for a fixed momentum transfer $\hbar\boldsymbol{\kappa}=2\pi\hbar\mathbf{k}$ from neutron to crystal as a function of energy transfer is found to consist of a number of δ-function peaks. These peaks are centered at the frequencies $\omega(\mathbf{k}j)$. The number of peaks in the cross section is determined by the energy and momentum conservation conditions which govern the scattering process. From measurements of the changes in the momenta and energies of the neutrons as a result of the scattering process the phonon dispersion curves $\omega=\omega(\mathbf{k}j)$ can be mapped out.

However, no crystal is perfectly harmonic. If we retain the cubic, quartic, $\cdots$, terms in the expansion of the crystal's potential energy in powers of the displacements of the atoms from their equilibrium positions we are dealing with what is called an anharmonic crystal. It is then found that the transformation which diagonalizes the harmonic part of the crystal Hamiltonian into a superposition of one mode harmonic oscillator Hamiltonians leads to coupling between these modes which is associated with the anharmonic terms in the potential energy. The study of the various thermal and dynamic properties of anharmonic crystals thus necessitates the solution of many-body problems.

Within the past several years the coherent scattering of neutrons by anharmonic crystals has been studied theoretically by several authors. The earliest work is that of van Hove[5] who gave a brief discussion of the scattering at the absolute zero of temperature. Van Hove's work was extended to finite temperatures by Kokkedee[6] who obtained an expression for the one-phonon coherent scattering cross section.

In his work Kokkedee retained anharmonic terms to all orders in the atomic displacements, and presented explicitly the contributions to the coherent scattering cross section from the cubic and quartic anharmonic terms. No attempt to evaluate the results of this analysis was made in this paper.

A different approach to this problem was made by Baym[7] who showed that the evaluation of the neutron scattering cross section could be reduced to the evaluation of the Fourier transform in space and time of a time-relaxed displacement-displacement correlation function, the phonon propagator. He did not, however, carry out a calculation of the propagator. Moreover, although Baym's result is exact for a harmonic crystal, it is only approximate for an anharmonic crystal. A calculation of the phonon propagator was carried out by Kashcheev and Krivoglaz[8] who solved the equation of motion it satisfies. However, these authors retained only cubic anharmonic terms in the crystal Hamiltonian so that their results are less complete than those of Kokkedee.

The effects of the anharmonic terms in the crystal's potential energy on the scattering of neutrons can be summarized qualitatively in the following way. Each of the harmonic normal mode frequencies $\omega(\mathbf{k}j)$, the unperturbed "single-particle" energies of the system, suffers a complex shift $\Delta\omega(\mathbf{k}j)+i\Gamma(\mathbf{k}j)$, the real part of which gives the change in the value of the frequency, and the imaginary part of which is the reciprocal of the lifetime of the single-particle amplitude for the phonon state described by $(\mathbf{k}j)$. Both parts are temperature dependent. The imaginary part of the shift shows up experimentally in the broadening of the peaks in the energy distribution of the scattered neutrons, and Γ is the half-width at half-maximum of the peak. The real part shows up as a shift in the center of the peak.

Both of these anharmonic effects have recently been observed experimentally. Larsson and co-workers[9] in Stockholm have measured phonon energy shifts and widths in aluminum, while similar measurements for phonons in lead have been made by Brockhouse and co-workers[10] at Chalk River.

In the present paper, we calculate the differential cross section for the scattering of neutrons by an anharmonic Bravais crystal. We consider only one-phonon processes and retain cubic and quartic anharmonic terms in the crystal Hamiltonian. The methods we use to carry out this calculation differ from those employed in the papers referred to above. In Sec. II we reduce the calculation of the scattering cross section to that of finding the Fourier transform in space and time of a time-relaxed displacement-displacement function. This reduction, however, is carried out in a manner which is quite different from that by which Baym achieves the same result; in particular, the method we use makes it easy to discuss, if desired, the higher order terms omitted from our, and from Baym's expression for the scattering cross section. In Sec. III our expression for the scattering cross section is manipulated into a form which can be evaluated through the use of a propagator technique similar to that employed

[5] L. van Hove, Technical Report No. 11, Solid State and Molecular Theory Group, Massachusetts Institute of Technology March 15, 1959 (unpublished). See also, L. van Hove, N. M. Hugenholtz, and L. P. Howland, *Quantum Theory of Many Particle Systems* (W. A. Benjamin, Inc., New York, 1961).

[6] J. Kokkedee, Physica **28**, 374 (1962).

[7] G. Baym, Phys. Rev. **121**, 741 (1961).

[8] V. N. Kashcheev and M. A. Krivoglaz, Soviet Phys.—Solid State **3**, 1107 (1961).

[9] K. E. Larsson, U. Dahlborg, and S. Holmryd, Arkiv Fysik **17**, 369 (1960).

[10] B. N. Brockhouse, T. Arase, G. Caglioti, M. Sakamoto, R. N. Sinclair, and A. D. B. Woods, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 531. See also, P. A. Egelstaff and S. McCallum, Nature **181**, 643 (1958).

by Luttinger and Ward[11] in their study of the interacting electron gas. The calculation of the phonon propagator in an anharmonic crystal is carried out in Sec. IV, and the formal result for the scattering cross section is obtained in Sec. V. The numerical evaluation of the real and imaginary parts of the complex shift in the phonon frequencies for a simple model of a three-dimensional crystal is described in Secs. VI and VII.

II. THE DIFFERENTIAL SCATTERING CROSS SECTION

Our starting point is an expression due to van Hove[12] for the differential scattering cross section per unit solid angle and unit interval of outgoing energy ϵ of the scattered neutron in the first Born approximation for coherent scattering:

$$\frac{d^2\sigma_{\rm coh}}{d\Omega d\epsilon}=\frac{a^2}{\hbar}\frac{q_1}{q_0}S(\boldsymbol{\kappa},\omega), \tag{2.1}$$

where

$$S(\boldsymbol{\kappa},\omega)=Z^{-1}\sum_i e^{-\beta E_i}\sum_j\langle E_i|\sum_l\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(l)]|E_j\rangle \times\langle E_j|\sum_{l'}\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(l')]|E_i\rangle\delta(\omega+(E_i-E_j)/\hbar). \tag{2.2}$$

In these equations $\mathbf{q}_0$ is the initial wave vector of the neutron and $\mathbf{q}_1=\mathbf{q}_0-\boldsymbol{\kappa}$ is its final wave vector.[13] $\hbar\omega$, which is equal to $(\hbar^2/2m)(q_0^2-q_1^2)$, is the energy transferred from the neutron to the crystal. a is the scattering length of the nuclei and $\mathbf{R}(l)$ is the instantaneous position vector of the lth atom in the crystal. $|E_i\rangle$ and $|E_j\rangle$ are energy eigenstates of the crystal Hamiltonian H, and Z is the crystal's partition function.

The position vector $\mathbf{R}(l)$ can be written as

$$\mathbf{R}(l)=\mathbf{x}(l)+\mathbf{u}(l), \tag{2.3}$$

where $\mathbf{x}(l)$ is the position vector of the mean position of the lth atom. It can be expressed as

$$\mathbf{x}(l)=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3, \tag{2.4}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the three primitive translation vectors of the crystal, and l_1, l_2, l_3 are three integers which are positive, negative, or zero. $\mathbf{u}(l)$ is the displacement of the lth atom away from its mean position.

If we use the Fourier integral representation for the δ function,

$$\delta(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{itx}, \tag{2.5}$$

we can rewrite Eq. (2.2) as

$$S(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\sum_{ll'}\exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\} \times\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)] \times\exp[i\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)]\rangle. \tag{2.6}$$

In this expression, we have introduced the Heisenberg operator

$$\mathbf{u}(l;t)=e^{i(t/\hbar)H}\mathbf{u}(l;0)e^{-i(t/\hbar)H}, \tag{2.7}$$

while the brackets $\langle\cdots\rangle$ denote the canonical ensemble average of the expectation value of an operator,

$$\langle O\rangle=Z^{-1}\sum_i e^{-\beta E_i}\langle E_i|O|E_i\rangle=\mathrm{Tr}e^{-\beta H}O/\mathrm{Tr}e^{-\beta H}. \tag{2.8}$$

The problem of evaluating $S(\boldsymbol{\kappa},\omega)$ becomes one of evaluating the correlation function $\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)] \times\exp[i\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)]\rangle$. At this point we can proceed in one of two ways. We can work with the correlation function as given, or we can manipulate it into a form in which simpler correlation functions appear. The former approach has been employed by van Hove[5] and by Kokkedee.[6] The latter has been used by Baym.[7] We follow the latter approach, but in a somewhat different form from that used by Baym.

Let us for the moment define new (noncommuting) operators x and y by

$$x=-i\boldsymbol{\kappa}\cdot\mathbf{u}(l;t),\quad y=i\boldsymbol{\kappa}\cdot\mathbf{u}(l';0). \tag{2.9}$$

Our problem thus becomes that of evaluating the function $\langle e^xe^y\rangle$. Since x and y do not commute it is not true any more that $e^xe^y=e^{x+y}$. But it is true that

$$e^xe^y=O_xe^{x+y}, \tag{2.10}$$

where O_x is an operator which orders all powers of x to the left of all powers of y. We now have to evaluate

$$\langle e^xe^y\rangle=\langle O_xe^{x+y}\rangle. \tag{2.11}$$

We now make use of cumulants[14] to express the right side of this equation as

$$\langle e^xe^y\rangle=\exp\sum_{n=1}^{\infty}\frac{1}{n!}(O_xM_n), \tag{2.12}$$

where the first few cumulants are given explicitly by

$$\begin{aligned}M_1&=\langle x+y\rangle,\\ M_2&=\langle(x+y)^2\rangle-\langle x+y\rangle^2,\\ M_3&=\langle(x+y)^3\rangle-3\langle(x+y)^2\rangle\langle x+y\rangle+2\langle x+y\rangle^3,\\ M_4&=\langle(x+y)^4\rangle-4\langle(x+y)^3\rangle\langle x+y\rangle-3\langle(x+y)^2\rangle^2\\ &\quad+12\langle(x+y)^2\rangle\langle x+y\rangle^2-6\langle x+y\rangle^4.\end{aligned} \tag{2.13}$$

In the case of Bravais lattices, it can be shown that

$$\langle x\rangle=\langle y\rangle=0. \tag{2.14}$$

This result follows in two steps. Firstly, from the invariance of a crystal against a rigid body translation through one of the translation vectors of the crystal, the thermal average $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle$ is independent of the unit cell index l. Moreover, since we are dealing with a time-independent system, $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle$ is also independent of t. Because of its independence of l, if $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle$ is

[11] J. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).
[12] L. van Hove, Phys. Rev. **95**, 249 (1954).
[13] The neutron wave vectors $\mathbf{q}_0$ and $\mathbf{q}_1$ are defined in such a way that their magnitudes equal 2π times the reciprocals of their wavelengths.
[14] M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics* (Charles Griffin and Company, Ltd., London, 1958) Chap. 3.

nonvanishing then it must correspond to a rigid body translation of the crystal as a whole. However, such a translation would contradict one of the conditions of equilibrium for an infinite crystal, or a crystal satisfying the cyclic boundary condition, viz., that there is no net force acting on any atom.[15] Therefore, $\langle \boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle$ must vanish. This result also holds for crystals with more than one atom per unit cell, provided that each atom is at a center of inversion symmetry.

Combining Eqs. (2.12), (2.13), and (2.14), we find that

$$\langle e^x e^y\rangle = \exp\{\tfrac{1}{2}\langle x^2+2xy+y^2\rangle + \tfrac{1}{6}\langle x^3+3x^2y+3xy^2+y^3\rangle + (1/24)[\langle x^4+4x^3y+6x^2y^2+4xy^3+y^4\rangle - 3\langle x^2+2xy+y^2\rangle^2]+\cdots\}. \quad (2.15)$$

If the thermal average were being carried out over the canonical ensemble for the harmonic crystal, then it is a well-known result that[16]

$$\langle e^x e^y\rangle_0 = \exp\{\tfrac{1}{2}\langle x^2+2xy+y^2\rangle_0\}. \quad (2.16)$$

This result means that if the terms past the first one on the right-hand side of Eq. (2.15) are nonvanishing, this can only be due to the anharmonic terms in the crystal's potential energy. That they are, in fact, nonvanishing follows from an actual calculation.

For a Bravais lattice, an average such as $\langle x^n\rangle$, or $\langle y^n\rangle$ is independent of the lattice position vectors $\mathbf{x}(l)$ and $\mathbf{x}(l')$, respectively, due to the translational invariance of the lattice. This result together with the defining equations, Eqs. (2.9), shows us that

$$\langle x^3\rangle = -\langle y^3\rangle. \quad (2.17)$$

We now factor the exponential function on the right side of Eq. (2.15) into

$$\langle e^x e^y\rangle = \exp\left\{\frac{1}{2}\langle x^2+y^2\rangle + \frac{1}{24}[\langle x^4\rangle - 3\langle x^2\rangle^2 + \langle y^4\rangle - 3\langle y^2\rangle^2]+\cdots\right\} \exp\left\{\langle xy\rangle + \tfrac{1}{2}\langle x^2y+xy^2\rangle + \frac{1}{24}\langle 4x^3y+6x^2y^2+4xy^3\rangle - \frac{1}{8}[4\langle xy\rangle^2 + 4\langle x^2\rangle\langle xy\rangle + 4\langle xy\rangle\langle y^2\rangle + 2\langle x^2\rangle\langle y^2\rangle]+\cdots\right\}. \quad (2.18)$$

The first factor in this expression does not describe the correlations between the displacements of the atoms at $\mathbf{x}(l)$ and $\mathbf{x}(l')$. It is, in fact, just the Debye-Waller factor corrected for anharmonic effects, and can be written explicitly as

$$e^{-2M} = \exp\{-\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle + \tfrac{1}{12}[\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^4\rangle - 3\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle^2]+\cdots\}. \quad (2.19)$$

[15] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 217.

[16] H. Ott, Ann. Physik 23, 169 (1935); M. Born, *Reports on Progress in Physics* (The Physical Society, London, 1942–43), Vol. 9, p. 294.

Since we have discussed the Debye-Waller factor in another paper[17] we omit further discussion of it here.

We are left with the second factor in Eq. (2.18) to consider. In terms of the displacements it becomes

$$\begin{aligned}\exp\{&\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &-\tfrac{1}{2}i[\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &-\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle] \\ &-\tfrac{1}{6}[\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &-3\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &+\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &-3\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &+3\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle^2 \\ &-\tfrac{3}{2}\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle \\ &+\tfrac{3}{2}\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\rangle\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle] \\ &+\cdots\}. \end{aligned} \quad (2.20)$$

All terms past the first in the exponent of this expression must be explicitly proportional to the anharmonic force constants, since they must vanish if the anharmonic forces are set equal to zero.

In the calculations that follow, we work only to the lowest nonvanishing order in the anharmonic force constants. This means that we can neglect all terms in the exponent in Eq. (2.20) past the leading term. This is the fundamental approximation of the present paper. It seems as if this is a quantitatively satisfactory approximation, if we can extrapolate the results of our Debye-Waller factor calculation to the present calculation. In reference 17 it was found that the contributions from the terms in square brackets in the exponent on the right side of Eq. (2.19) are at least two orders of magnitude smaller than the anharmonic contributions to the average $\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle$. We expect that a similar result holds for the time-relaxed correlation functions in Eq. (2.21). We thus find that

$$\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)]\rangle \cong e^{-2M}\exp[\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle]. \quad (2.21)$$

This is Baym's result.[7] Equation (2.20) shows explicitly what kinds of terms are omitted in his analysis through the linearization of a functional differential equation which appears in his treatment, and provides a starting point for a more accurate theory.

If we substitute Eq. (2.21) into Eq. (2.6) we obtain

$$S(\boldsymbol{\kappa},\omega) = \frac{e^{-2M}}{2\pi}\sum_{ll'}\exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\} + \int_{-\infty}^{\infty} dt\, e^{i\omega t}\exp[\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle]. \quad (2.22)$$

In the harmonic approximation Eq. (2.22) is exact, provided that $2M$ and $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle$ are replaced by $2M_0$ and $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle_0$ where the thermal

[17] A. A. Maradudin and P. A. Flinn (to be published).

averages are evaluated in the canonical ensemble of the harmonic crystal. If we expand $\exp\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle_0$ in powers of its argument in the equation analogous to Eq. (2.22), the contribution to $S(\boldsymbol{\kappa},\omega)$ from the term containing $(1/n!)\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle_0^n$ gives rigorously the cross section for the scattering events in which the neutron excites and de-excites a total of n quanta of vibrational energy. Kokkedee[6] has pointed out that in the case of an anharmonic crystal it is no longer possible to write a similar expansion for the scattering cross section in which the nth term rigorously describes the n-phonon processes: The various processes are now generally mixed up in a complicated way. This means that it is no longer rigorously possible to effect a separation of the scattering cross section into one-phonon peaks plus a multiphonon background: The peaks describe parts of the background as well. Nevertheless, if in Eq. (2.22) we expand $\exp\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle$ in powers of its argument and keep just the first two terms, then as long as $\Gamma(\mathbf{k}j)$ is small compared to $\omega(\mathbf{k}j)$ we can still identify the term containing $\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle$ to the first power as the dominant contribution to the "one-phonon" peaks in the scattering cross section. The terms in Eq. (2.20) we have neglected in writing Eq. (2.22) will give rise to higher order corrections to these peaks. The condition $\Gamma(\mathbf{k}j)\ll\omega(\mathbf{k}j)$ is not overly restrictive, since if $\Gamma(\mathbf{k}j)$ is comparable with $\omega(\mathbf{k}j)$, the "one-phonon" peaks would not be distinguishable from the background. The experimental results of Larsson *et al.*[9] and Brockhouse *et al.*[10] show that in the cases they have studied these peaks are generally resolvable.

The first two terms in the expansion of $S(\boldsymbol{\kappa},\omega)$ written out explicitly are

$$S(\boldsymbol{\kappa},\omega)=S_0(\boldsymbol{\kappa},\omega)+S_1(\boldsymbol{\kappa},\omega)+\cdots, \tag{2.23}$$

where[17a]

$$S_0(\boldsymbol{\kappa},\omega)=e^{-2M}\delta(\omega)\sum_{ll'}\exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}$$

$$=N^2e^{-2M}\delta(\omega)\Delta(\boldsymbol{\kappa}/2\pi) \tag{2.24}*$$

and

$$S_1(\boldsymbol{\kappa},\omega)=\frac{e^{-2M}}{2\pi}\sum_{ll'}\exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}$$

$$\times\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\boldsymbol{\kappa}\cdot\mathbf{u}(l;t)\boldsymbol{\kappa}\cdot\mathbf{u}(l';0)\rangle. \tag{2.25}$$

The term $S_0(\boldsymbol{\kappa},\omega)$ is seen to describe the coherent elastic scattering of neutrons. It is elastic because of the factor $\delta(\omega)$, and it is coherent because of the factor $\Delta(\boldsymbol{\kappa}/2\pi)$, which expresses the Bragg condition. The term $S_1(\boldsymbol{\kappa},\omega)$ describes the situation of interest to us, coherent, inelastic scattering of neutrons by one-phonon processes. It is with the evaluation of $S_1(\boldsymbol{\kappa},\omega)$ that we will be concerned in the remainder of this paper.

[17a] The function $\Delta(\mathbf{k})$ equals unity if $\mathbf{k}$ equals a translation vector of the reciprocal lattice, and vanishes otherwise.

III. THE ONE-PHONON SCATTERING CROSS SECTION

If we introduce a function $B_{xy}(ll';\omega)$ by

$$B_{xy}(ll';\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle u_x(l;t)u_y(l';0)\rangle, \tag{3.1}$$

then in terms of this function the one-phonon scattering cross section $S_1(\boldsymbol{\kappa},\omega)$ is given by

$$S_1(\boldsymbol{\kappa},\omega)=\frac{e^{-2M}}{2\pi}\sum_{ll'}\sum_{xy}\exp\{-i\boldsymbol{\kappa}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]\}\times\kappa_xB_{xy}(ll';\omega)\kappa_y. \tag{3.2}$$

In this section we obtain an expression for $B_{xy}(ll';\omega)$ which is well suited for its evaluation.

We begin by introducing the auxiliary function

$$A_{xy}(ll';\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle[u_x(l;t),u_y(l';0)]\rangle. \tag{3.3}$$

If we express the thermal average in this expression explicitly, using Eqs. (2.7) and (2.8), then with the aid of the cyclic theorem for traces and Cauchy's integral formula it is straightforward to show that the relation between $B_{xy}(ll';\omega)$ and $A_{xy}(ll';\omega)$ is given by

$$B_{xy}(ll';\omega)=A_{xy}(ll';\omega)/(1-e^{-\beta\hbar\omega}). \tag{3.4}$$

Since the operator $u_x(l;0)$ is Hermitian (it is real, in fact), we have the result that

$$\langle[u_x(l;t),u_y(l';0)]\rangle=2i\,\mathrm{Im}\langle u_x(l;t)u_y(l';0)\rangle. \tag{3.5}$$

Moreover, since the Hamiltonian operator for the anharmonic crystal written in terms of momenta and displacements is real, we can choose the eigenstates of H to be real, with no loss of generality, since the trace is invariant against representation. We then find that $\mathrm{Im}\langle u_x(l;t)u_y(l';0)\rangle$ is an odd function of t. The equation (3.3) for $A_{xy}(ll';\omega)$ thus becomes

$$A_{xy}(ll';\omega)=-4\,\mathrm{Im}\int_0^{\infty}dt\,\sin\omega t\langle u_x(l;t)u_y(l';0)\rangle. \tag{3.6}$$

Let us expand the correlation function in Eq. (3.6) in terms of the eigenstates of H. The expression for $A_{xy}(ll';\omega)$ can be then written

$$\begin{aligned}A_{xy}(ll';\omega)&=-4\lim_{\epsilon\to0+}\mathrm{Im}\int_0^{\infty}dt\,e^{-\epsilon t}\sin\omega t\{Z^{-1}\sum_{mn}e^{-\beta E_m}\\&\quad\times e^{i(t/\hbar)(E_m-E_n)}\langle E_m|u_x(l;0)|E_n\rangle\\&\quad\times\langle E_n|u_y(l';0)|E_m\rangle\}\\&=2\pi[\rho(-\omega)-\rho(\omega)],\end{aligned} \tag{3.7}$$

where

$$\rho(\omega)=\frac{1}{Z}\sum_{mn}e^{-\beta E_m}\langle E_m|u_x(l;0)|E_n\rangle\times\langle E_n|u_y(l';0)|E_m\rangle\delta(\omega-(1/\hbar)(E_m-E_n)). \tag{3.8}$$

If we now make use of the fact that $\langle E_m|u_x(l;0)|E_n\rangle$ is real and symmetric

$$\langle E_m|u_x(l;0)|E_n\rangle=\langle E_n|u_x(l;0)|E_m\rangle,$$

then it readily follows from the definition, Eq. (3.8), that

$$\rho(-\omega)=e^{\beta\hbar\omega}\rho(\omega), \tag{3.9}$$

so that combining Eqs. (3.4), (3.7), and (3.9) we obtain

$$B_{xy}(ll';\omega)=2\pi e^{\beta\hbar\omega}\rho(\omega). \tag{3.10}$$

It is thus only necessary to determine the function $\rho(\omega)$.

This we do in the following way.[18] We introduce the function

$$f(u)=\langle Te^{uH}u_x(l;0)e^{-uH}u_y(l';0)\rangle \equiv\langle Tu_x(l;u)u_y(l';0)\rangle, \tag{3.11}$$

where u is real, and T is the time ordering operator which orders a product of time-dependent operators in order of increasing times from right to left. Thus, we have that

$$\begin{aligned}\langle Tu_x(l;u_1)u_y(l';u_2)\rangle &=\langle u_x(l;u_1)u_y(l';u_2)\rangle, \quad u_1>u_2\\ &=\langle u_y(l';u_2)u_x(l;u_1)\rangle, \quad u_2>u_1.\end{aligned} \tag{3.12}$$

The motivation for working with $f(u)$ is that we can treat the reciprocal temperature β and the "time" u on the same footing without the complications which arise if we work in a complex temperature-time space.[19] This is convenient, and after all it is really the spectral function $\rho(\omega)$ rather than the correlation function $\langle u_x(l;t)u_y(l';0)\rangle$ that we require.

Let us write $f(u)$ explicitly as

$$\begin{aligned}f(u)&=Z^{-1}\,\mathrm{Tr}e^{-\beta H}e^{uH}u_x(l;0)e^{-uH}u_y(l';0), \quad u>0\\ &=Z^{-1}\,\mathrm{Tr}e^{-\beta H}u_y(l';0)e^{uH}u_x(l;0)e^{-uH}, \quad u<0.\end{aligned} \tag{3.13}$$

It then follows with the aid of the cyclic theorem for traces that

$$f(u+\beta)=f(u), \quad -\beta<u<0. \tag{3.14}$$

This means that we only need to know $f(u)$ for u in the interval $-\beta<u<0$ and we can determine it outside this interval with the aid of Eq. (3.14).

This result suggests that we expand $f(u)$ in a Fourier series which is periodic with a period β:

$$f(u)=\sum_{l=-\infty}^{\infty}a_l e^{2\pi ilu/\beta}. \tag{3.15}$$

The Fourier coefficients are given by

$$\begin{aligned}a_l&=\frac{1}{\beta}\int_0^\beta f(u)e^{-2\pi ilu/\beta}du\\ &=\frac{1}{\beta\hbar Z}\sum_{mn}e^{-\beta E_m}\langle E_m|u_x(l;0)|E_n\rangle\langle E_n|u_y(l';0)|E_m\rangle\\ &\quad\times\frac{e^{\beta(E_m-E_n)}-1}{(1/\hbar)(E_m-E_n)-2\pi il/\beta\hbar}.\end{aligned} \tag{3.16}$$

We now introduce a function of a continuous variable $a(\nu)$ which equals a_l when

$$\nu=\nu_l=2\pi il/\beta\hbar. \tag{3.17}$$

To specify $a(\nu)$ completely, we require that it have a branch cut along the real axis, be analytic everywhere else in the complex ν plane, and go to zero as ν approaches infinity along any straight line in the upper or lower half-plane.[20] We see from Eq. (3.16) that we can obtain $a(\nu)$ simply by replacing the discrete variable $2\pi il/\beta\hbar$ by ν. Thus, $a(\nu)$ is given by

$$\begin{aligned}a(\nu)=\frac{1}{\beta\hbar Z}\sum_{mn}e^{-\beta E_m}(e^{\beta(E_m-E_n)}-1)\langle E_m|u_x(l;0)|E_n\rangle\\ \times\langle E_n|u_y(l';0)|E_m\rangle\frac{1}{(1/\hbar)(E_m-E_n)-\nu}.\end{aligned} \tag{3.18}$$

Consequently we see that

$$\lim_{\epsilon\to0+}\frac{a(\nu+i\epsilon)-a(\nu-i\epsilon)}{2\pi i}=\frac{1}{\beta\hbar}(e^{\beta\hbar\nu}-1)\rho(\nu),$$

so that

$$\rho(\nu)=\frac{\beta\hbar}{e^{\beta\hbar\nu}-1}\frac{1}{2\pi i}\lim_{\epsilon\to0+}[a(\nu+i\epsilon)-a(\nu-i\epsilon)]. \tag{3.19}$$

Comparing Eqs. (3.16) and (3.24) we finally obtain the desired result

$$B_{xy}(ll';\omega)=\frac{2\pi\beta\hbar}{1-e^{-\beta\hbar\omega}}\lim_{\epsilon\to0+}\frac{a(\omega+i\epsilon)-a(\omega-i\epsilon)}{2\pi i}. \tag{3.20}$$

The special advantage of Eq. (3.20) as the starting point for our calculations is that, as we shall see, a comparatively simple procedure exists for the determination of the Fourier coefficients $\{a_l\}$ and hence the function $a(\nu)$.

IV. THE PHONON PROPAGATOR

To evaluate the Fourier coefficients of the function $f(u)$ which is defined by Eq. (3.11) we first express $f(u)$ in terms of phonon creation and destruction

[18] See, for example, the review article by A. I. Alekseev, Soviet Phys.—Uspekhi 4, 23 (1961). The application of this method to the present problem, however, was stimulated by a recent paper by J. S. Langer, Phys. Rev. 127, 5 (1962), in which this method is used in the calculation of the electrical conductivity of the interacting electron gas in the presence of randomly distributed impurities.

[19] E. W. Montroll and J. C. Ward, Physica 25, 423 (1959).

[20] G. Baym and N. D. Mermin, J. Math. Phys. 2, 232 (1961).

operators. We expand $u_x(l;0)=u_x(l)$ as

$$u_x(l)=\left(\frac{\hbar}{2NM}\right)^{1/2}\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)}{[\omega(\mathbf{k}j)]^{1/2}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)}\times(a_{-\mathbf{k}j}^{\dagger}+a_{\mathbf{k}j}). \quad (4.1)$$

In this expression, M is the atomic mass, and N is the number of atoms in the crystal. $\omega(\mathbf{k}j)$ is the frequency of the normal mode described by the wave vector $\mathbf{k}$ and polarization index j. $e(\mathbf{k}j)$ is the polarization vector for the mode $(\mathbf{k}j)$. The allowed values of $\mathbf{k}$ are uniformly and densely distributed throughout a unit cell of the reciprocal lattice, or equivalently, throughout the first Brillouin zone of the lattice. The polarization index j takes the values $j=1, 2, 3$. The operators $a_{\mathbf{k}j}^{\dagger}$ and $a_{\mathbf{k}j}$ are phonon creation and destruction operators, respectively.

If we substitute Eq. (4.1) into Eq. (3.11), the expression for $f(u)$ becomes

$$f(u)=\frac{\hbar}{2NM}\sum_{\mathbf{k}\mathbf{k}',jj'}\frac{e_x(\mathbf{k}j)e_x(\mathbf{k}'j')}{[\omega(\mathbf{k}j)\omega(\mathbf{k}'j')]^{1/2}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l)-2\pi i\mathbf{k}'\cdot\mathbf{x}(l')}\times\langle Te^{uH}(a_{-\mathbf{k}j}^{\dagger}+a_{\mathbf{k}j})e^{-uH}(a_{-\mathbf{k}'j'}+a_{\mathbf{k}'j'}^{\dagger})\rangle. \quad (4.2)$$

We are thus required to find the Fourier coefficients of the correlation function

$$\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)=\langle Te^{uH}(a_{-\mathbf{k}j}^{\dagger}+a_{\mathbf{k}j})e^{-uH}(a_{-\mathbf{k}'j'}+a_{\mathbf{k}'j'}^{\dagger})\rangle. \quad (4.3)$$

The Fourier coefficient of this function, which we denote by $A_l(\mathbf{k}j;\mathbf{k}'j')$, is given by

$$A_l(\mathbf{k}j;\mathbf{k}'j')=\frac{1}{\beta}\int_0^{\beta}\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)e^{-2\pi ilu/\beta}du. \quad (4.4)$$

We call this Fourier coefficient the phonon propagator.

The Hamiltonian of the anharmonic crystal expressed in terms of creation and destruction operators is (omitting the zero-point energy)

$$\begin{aligned}H=&\sum_{\mathbf{k},j}\hbar\omega(\mathbf{k}j)a_{\mathbf{k}j}^{\dagger}a_{\mathbf{k}j}\\&+\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}V^{(3)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)(a_{-\mathbf{k}_1j_1}^{\dagger}+a_{\mathbf{k}_1j_1})\\&\times(a_{-\mathbf{k}_2j_2}^{\dagger}+a_{\mathbf{k}_2j_2})(a_{-\mathbf{k}_3j_3}^{\dagger}+a_{\mathbf{k}_3j_3})\\&+\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}V^{(4)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)\\&+(a_{-\mathbf{k}_1j_1}^{\dagger}+a_{\mathbf{k}_1j_1})(a_{-\mathbf{k}_2j_2}^{\dagger}+a_{\mathbf{k}_2j_2})(a_{-\mathbf{k}_3j_3}^{\dagger}+a_{\mathbf{k}_3j_3})\\&\times(a_{-\mathbf{k}_4j_4}^{\dagger}+a_{\mathbf{k}_4j_4})+\cdots\\=&H_0+H_A. \quad (4.5)\end{aligned}$$

In what follows we retain only the cubic and quartic terms in the anharmonic Hamiltonian H_A.

The $V^{(n)}$ coefficients which appear in the anharmonic Hamiltonian are the Fourier transforms of the nth order atomic force constants. They are completely symmetric in the indices $(\mathbf{k}_ij_i)$, and they are related to the analogous coefficients defined by Born and Huang[15] by

$$V^{(3)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)=\frac{\hbar^{3/2}}{2^{3/2}\times6N^{1/2}}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\times\frac{\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)}{[\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)\omega(\mathbf{k}_3j_3)]^{1/2}}, \quad (4.6a)$$

$$V^{(4)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)=\frac{\hbar^2}{2^2\times24N}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4)\times\frac{\Phi(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)}{[\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)\omega(\mathbf{k}_3j_3)\omega(\mathbf{k}_4j_4)]^{1/2}}. \quad (4.6b)$$

Instead of working with the usual phonon creation and destruction operators we find it convenient to introduce new phonon operators by

$$A_{\mathbf{k}j}=a_{-\mathbf{k}j}^{\dagger}+a_{\mathbf{k}j}, \quad (4.7a)$$

$$A_{-\mathbf{k}j}=a_{\mathbf{k}j}^{\dagger}+a_{-\mathbf{k}j}=A_{\mathbf{k}j}^{\dagger}. \quad (4.7b)$$

In terms of these operators the function $\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)$ becomes

$$\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)=\langle TA_{\mathbf{k}j}(u)A_{\mathbf{k}'j'}^{\dagger}(0)\rangle, \quad (4.6)$$

where

$$A_{\mathbf{k}j}(u)=e^{uH}A_{\mathbf{k}j}(0)e^{-uH}. \quad (4.7)$$

The motivation for introducing these new operators is that both the desired correlation function and the anharmonic Hamiltonian have a simple form when expressed in terms of them, and our calculations are accordingly simplified. We find that

$$H_A=\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}V^{(3)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}A_{\mathbf{k}_3j_3}+\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}\sum_{j_1j_2j_3j_4}V^{(4)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)\times A_{\mathbf{k}_1j_1}A_{\mathbf{k}_2j_2}A_{\mathbf{k}_3j_3}A_{\mathbf{k}_4j_4}+\cdots. \quad (4.8)$$

Van Hove[5] has pointed out that in general the expectation value of the nth order potential energy term in the crystal Hamiltonian is of the order of magnitude of $\hbar\omega(u/r_0)^{n-2}$ per unit volume. Here ω is some mean vibrational frequency of the crystal, u is a mean (or preferably, a root mean square) atomic displacement, and r_0 is the nearest-neighbor separation in the crystal. This means that if we denote (u/r_0) by λ we can write the anharmonic Hamiltonian schematically as

$$H_A=\lambda V_3+\lambda^2V_4+\cdots, \quad (4.9)$$

and this result provides a basis for ordering the various contributions to $\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)$ and hence to $A_l(\mathbf{k}j;\mathbf{k}'j')$ as to their magnitude.

The evaluation of $A_l(\mathbf{k}j;\mathbf{k}'j')$ has been described in great detail by one of the authors,[21] and we will merely outline the procedure used here. Our starting point is the expansion

$$\mathfrak{F}(\mathbf{k}j;\mathbf{k}'j';u)=\Big\langle T\tilde{A}_{\mathbf{k}j}(u)\tilde{A}_{\mathbf{k}'j'}{}^{\dagger}(0)\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\times\int_0^\beta d\beta_1\cdots\int_0^\beta d\beta_n\,\tilde{H}_A(\beta_1)\cdots\tilde{H}_A(\beta_n)\Big\rangle_{0c},\quad(4.10)$$

where $\tilde{O}(\beta)$ is an operator in the interaction representation,

$$\tilde{O}(\beta)=e^{\beta H_0}Oe^{-\beta H_0}.\quad(4.11)$$

The notation $\langle\cdots\rangle_{0c}$ means that the average of the expression enclosed in the brackets is evaluated in the canonical ensemble of the harmonic crystal, and that only contributions associated with connected diagrams are retained in the expansion. In evaluating the indicated thermal average it is only necessary to pair the $\tilde{A}$ operators two by two different in all possible ways. In drawing diagrams to represent the contributions from the various terms in Eq. (4.10), we can order the vertices corresponding to the three- and four-phonon interactions from bottom to top in order of increasing times. Each pairing of two $\tilde{A}$ operators can then be represented by a solid line joining the corresponding vertices.

The two steps of taking the thermal average and evaluating the integrals over the β's are simplified if we introduce the function

$$g_{\mathbf{k}j}(u)=\langle T\tilde{A}_{\mathbf{k}j}{}^{\dagger}(u)\tilde{A}_{\mathbf{k}j}(0)\rangle_0=n(\mathbf{k}j)e^{|u|\hbar\omega(\mathbf{k}j)}+[n(\mathbf{k}j)+1]e^{-|u|\hbar\omega(\mathbf{k}j)}=\langle T\tilde{A}_{\mathbf{k}j}(u)\tilde{A}_{\mathbf{k}j}{}^{\dagger}(0)\rangle.\quad(4.12)$$

All other averages of a product of two time-ordered $\tilde{A}$ operators vanish. In Eq. (4.12)

$$n(\mathbf{k}j)=\{\exp[\beta\hbar\omega(\mathbf{k}j)]-1\}^{-1}$$

is the mean phonon occupation number. Equation (4.12) also has the consequence that in drawing diagrams it is not necessary to direct the phonon lines, as would be the case if we were working with the a operators. The function $g_{\mathbf{k}j}(u)$ in addition to being an even function of u also satisfies the condition

$$g_{\mathbf{k}j}(u+\beta)=g_{\mathbf{k}j}(u),\quad -\beta<u<0.\quad(4.13)$$

It possesses a simple Fourier series expansion

$$g_{\mathbf{k}j}(u)=\frac{2\omega(\mathbf{k}j)}{\beta\hbar}\sum_{l=-\infty}^{\infty}\frac{e^{2\pi ilu/\beta}}{\omega_l{}^2+\omega^2(\mathbf{k}j)}=\sum_{l=-\infty}^{\infty}a_l(\mathbf{k}j)e^{2\pi ilu/\beta},\quad(4.14)$$

where

$$\omega_l=2\pi l/\beta\hbar.\quad(4.15)$$

We shall refer to $a_l(\mathbf{k}j)$ as the free phonon propagator. Note that it is an even function of l.

When the expansion (4.14) is substituted into Eq. (4.10) the integrals over the β variables can be carried out directly with the aid of the result

$$\int_0^\beta dx\,e^{2\pi ilx/\beta}=\beta\delta_{l0}\quad(4.16)$$

for l an integer. The result is a function which depends on u in the form $e^{2\pi ilu/\beta}$, so that its Fourier coefficient $A_l(\mathbf{k}j;\mathbf{k}'j')$ can be read off simply.

It is found that the phonon propagator $A_l(\mathbf{k}j;\mathbf{k}'j')$ is diagonal in $\mathbf{k}$ and $\mathbf{k}'$, that is,

$$A_l(\mathbf{k}j;\mathbf{k}'j')=\Delta(\mathbf{k}-\mathbf{k}')A_l(\mathbf{k}jj').\quad(4.17)$$

This result is a consequence of the invariance of the crystal against a rigid body displacement through one of its translation vectors. This invariance means that the function $B_{xy}(ll';\omega)$ can depend on the vectors $\mathbf{x}(l)$ and $\mathbf{x}(l')$ only through their difference. In view of Eq. (4.2) this means that $\mathbf{k}=\mathbf{k}'$. The fact that the polarization index j' does not necessarily have to equal j is referred to as "polarization mixing."

We can now summarize the rules for computing the nth order contribution to the Fourier coefficient $A_l(\mathbf{k}jj')$.

(1) Draw all topologically distinct connected nth-order diagrams in which a free phonon line labeled by $(\mathbf{k}j)$ enters from the bottom of the page and a free phonon line labeled $(\mathbf{k}j')$ leaves at the top of the page. Although it is not necessary to direct the phonon lines, it is convenient to direct all lines up.

(2) With each phonon line labeled $(\mathbf{k}j)$ associate a factor

$$a_l(\mathbf{k}j)=\frac{2\omega(\mathbf{k}j)}{\beta\hbar}\frac{1}{\omega_l{}^2+\omega^2(\mathbf{k}j)},\quad \omega_l=\frac{2\pi l}{\beta\hbar}.$$

(3) At each vertex conserve the $\mathbf{k}$ vectors according to the rule that the sum of the wave vectors for lines leaving a vertex equals the sum of the wave vectors entering the vertex (modulo a reciprocal lattice vector).

(4) At each vertex conserve the ω_l's according to the rule that the sum of the ω_l's leaving a vertex equals the sum of the ω_l's entering a vertex.

(5) At each vertex insert the appropriate matrix element.

(6) Insert a factor $[(-1)^n/n!]\beta^n$, where the β^n comes from the integrations over the n β-variables.

(7) Insert a combinatorial factor which gives the number of pairing schemes to which the diagram corresponds. This factor is the product of the number of topologically equivalent diagrams that can be drawn for a fixed arrangement of the vertices, the number of

[21] A. A. Maradudin, lecture notes, Physics Department, Carnegie Institute of Technology, 1962 (unpublished), Vol. II.

different labelings of the $(\mathbf{k}_i j_i)$ at each vertex for each pairing scheme, and the number of ways of permuting the order of the three- and four-phonon vertices.

(8) Finally, sum over the independent $\mathbf{k}$'s, j's, and l's.

The diagrams which contribute to the Fourier coefficient $A_l(\mathbf{k}jj')$ are of the following type. A free phonon line $(\mathbf{k}j)$ enters, "things of arbitrary complexity happen,"[11] and a free phonon line $(\mathbf{k}j')$ emerges. The sum of the contributions from all such diagrams calculated according to the rules of the preceding paragraphs gives the coefficient $A_l(\mathbf{k}jj')$. The general form of these diagrams is shown in Fig. 1(a). Such diagrams fall into two categories, *improper* and *proper*. A diagram is called improper if it can be separated into two parts by cutting a free phonon line. A diagram is called proper if it cannot be separated into two parts in this way. The Fourier coefficient $A_l(\mathbf{k}jj')$ can be expressed in terms of contributions from proper diagrams only. The contributions to $A_l(\mathbf{k}jj')$ from all possible proper diagrams is indicated diagrammatically in Fig. 1(b) and is given explicitly by

$$a_l(\mathbf{k}j)G_l(\mathbf{k}jj')a_l(\mathbf{k}j'),$$

where $G_l(\mathbf{k}jj')$ is a function which is called the *proper self-energy*. The contribution to $A_l(\mathbf{k}jj')$ from all improper diagrams which separate into exactly two proper diagrams if we cut a single free phonon line is

$$\sum_{j_1} a_l(\mathbf{k}j)G_l(\mathbf{k}jj_1)a_l(\mathbf{k}j_1)G_l(\mathbf{k}j_1j')a_l(\mathbf{k}j').$$

Proceeding in this way we obtain

$$\begin{aligned}A_l(\mathbf{k}jj')=&\delta_{jj'}a_l(\mathbf{k}j)\\&+a_l(\mathbf{k}j)G_l(\mathbf{k}jj')a_l(\mathbf{k}j')+a_l(\mathbf{k}j)\\&\times\sum_{j_1}G_l(\mathbf{k}jj_1)a_l(\mathbf{k}j_1)G_l(\mathbf{k}j_1j')a_l(\mathbf{k}j')+\cdots.\end{aligned}\quad(4.18)$$

We see that this expansion is nothing more than the iteration solution to the 3×3 matrix equation

$$\begin{aligned}A_l(\mathbf{k}jj')=&\delta_{jj'}a_l(\mathbf{k}j)\\&+a_l(\mathbf{k}j)\sum_{j_1}G_l(\mathbf{k}jj_1)A_l(\mathbf{k}j_1j'),\\&(j,j'=1,2,3).\end{aligned}\quad(4.19)$$

This equation is called the Dyson equation for the phonon propagator. If it were not for polarization mixing this equation would be a simple linear algebraic equation whose solution could be written down immediately.

In general, the set of equations (4.19) would have to be solved numerically. However, in order for the results of this section to be most useful it is desirable to have an analytic solution of these equations even if this solution is an approximate one. Such a solution can be achieved in the following way. We rewrite Eq. (4.19) as

$$\sum_{j_1}\{\delta_{jj_1}-a_l(\mathbf{k}j)G_l(\mathbf{k}jj_1)\}A_l(\mathbf{k}j_1j')=\delta_{jj'}a_l(\mathbf{k}j).\quad(4.20)$$

Let us now separate the matrix $G_l(\mathbf{k}jj')$ into its diagonal and nondiagonal parts:

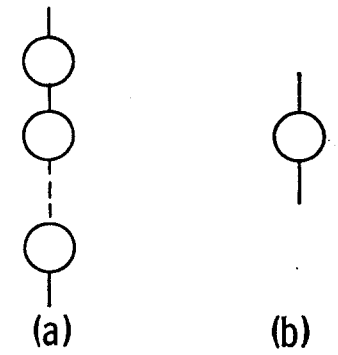

FIG. 1. (a) A schematic representation of a typical (improper) diagram which contributes to the phonon propagator. (b) A schematic representation of proper diagram which contributes to the phonon propagator.

$$G_l(\mathbf{k}jj')=\delta_{jj'}G_l(\mathbf{k}j)+G_l{}^N(\mathbf{k}jj'),\quad(4.21)$$

where $G_l{}^N(\mathbf{k}jj)=0$. Then Eq. (4.20) becomes

$$\begin{aligned}&\sum_{j_1}\delta_{jj_1}\{1-a_l(\mathbf{k}j)G_l(\mathbf{k}j)\}A_l(\mathbf{k}j_1j')\\&\quad=\delta_{jj'}a_l(\mathbf{k}j)+\sum_{j_1}a_l(\mathbf{k}j)G_l{}^N(\mathbf{k}jj_1)A_l(\mathbf{k}j_1j').\end{aligned}\quad(4.22)$$

We can now solve this equation by iteration. To second order we obtain

$$\begin{aligned}A_l(\mathbf{k}jj')=&\frac{\delta_{jj'}}{a_l{}^{-1}(\mathbf{k}j)-G_l(\mathbf{k}j)}+\frac{1}{a_l{}^{-1}(\mathbf{k}j)-G_l(\mathbf{k}j)}\\&\times G_l{}^N(\mathbf{k}jj')\frac{1}{a_l{}^{-1}(\mathbf{k}j')-G_l(\mathbf{k}j')}+\cdots.\end{aligned}\quad(4.23)$$

In the present case, $G_l(\mathbf{k}jj')$ is at least $O(\lambda^2)$, so that if we are satisfied with a result which is correct to lowest order in the anharmonic force constants, we may write

$$\begin{aligned}A_l(\mathbf{k}jj')\cong&\delta_{jj'}\frac{2\omega(\mathbf{k}j)}{\beta\hbar}\\&\times\frac{1}{\omega_l{}^2+\omega^2(\mathbf{k}j)-[2\omega(\mathbf{k}j)/\beta\hbar]G_l(\mathbf{k}j)}.\end{aligned}\quad(4.24)$$

For some purposes, it is convenient to effect an approximate partial fractions decomposition of the expression for $A_l(\mathbf{k}jj')$ given by Eq. (4.24). To lowest order in the anharmonic force constants, we obtain

$$\begin{aligned}A_l(\mathbf{k}jj')\cong&\delta_{jj'}\frac{1}{\beta\hbar}\Big\{\frac{1}{i\omega_l+\omega(\mathbf{k}j)-(1/\beta\hbar)G_l(\mathbf{k}j)}\\&+\frac{1}{-i\omega_l+\omega(\mathbf{k}j)-(1/\beta\hbar)G_l(\mathbf{k}j)}\Big\}.\end{aligned}\quad(4.25)$$

When $A_l(\mathbf{k}jj')$ is written in this way, we see why $G_l(\mathbf{k}jj')$ is called a self-energy. Its diagonal part has the effect of altering the frequency $\omega(\mathbf{k}j)$ and hence the energy of the phonon in the mode $(\mathbf{k}j)$.

It should be pointed out that the second term on the right side of Eq. (4.23) has no diagonal elements, i.e., $j'\neq j$. This means that for those problems in which

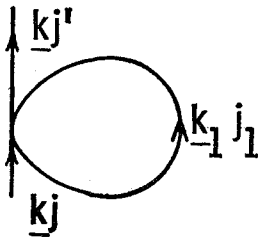

FIG. 2. The first-order diagram which contributes to the proper self-energy to $O(\lambda^2)$.

only the diagonal elements of $A_l(\mathbf{k}jj')$ are required, as for example in calculating the optical absorption coefficient of an ionic crystal, the result given by Eq. (4.24) is quite a good approximation since the corrections in this case are $O(\lambda^4)$.

We now turn to a closer look at the proper self-energy. By definition $G_l(\mathbf{k}jj')$ is the sum of contributions from all subdiagrams (past zeroth order) in the expansion of $A_l(\mathbf{k}jj')$ that cannot be divided into two parts by cutting one free phonon line, and which have no free phonon lines entering or leaving the diagram.

In first order, the only contribution to $G_l(\mathbf{k}jj')$ comes from the diagram shown in Fig. 2. Its value calculated according to the rules stated above is given by

$$G_l^{(1)}(\mathbf{k}jj') = -12\beta \sum_{\mathbf{k}_1,j_1} \sum_{l_1} V^{(4)}(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1) \times a_{l_1}(\mathbf{k}_1j_1). \quad (4.26)$$

The factor of 12 multiplying the sums arises from the fact that the phonon $(\mathbf{k}j)$ can pair with any one of the

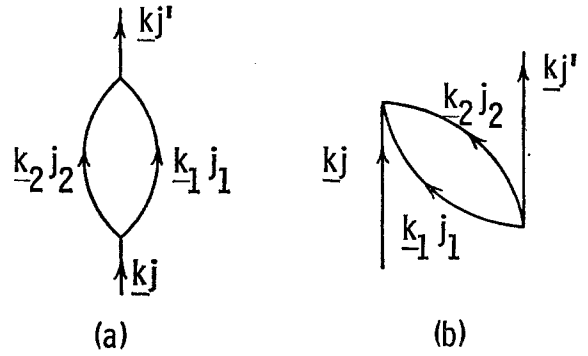

FIG. 3. The two second-order diagrams which contribute to the proper self-energy to $O(\lambda^2)$.

four phonons associated with the four-phonon vertex, while the phonon $(\mathbf{k}j')$ can pair with any of the remaining three phonons. Since the matrix element $V^{(4)}(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)$ is completely symmetric in the $(\mathbf{k}_ij_i)$ each of the 12 possible pairing schemes gives the same contribution to $G_l^{(1)}(\mathbf{k}jj')$. The loop at the four-phonon vertex in the diagram in Fig. 2 describes a situation in which a phonon is created and absorbed at the same vertex. Such phonons are called *instantaneous phonons*.

It should be remarked that in a Bravais crystal instantaneous phonons can occur only at four phonon vertices as long as we retain only cubic and quartic anharmonic terms in the crystal Hamiltonian. Instantaneous phonons at a three-phonon vertex have associated with them a diagram fragment of the type shown in Fig. 4. The matrix element associated with such a vertex has the form $V^{(3)}(\mathbf{k}_1j_1;-\mathbf{k}_2j_2;\mathbf{k}_2j_2)$, and it can be shown[22] that this matrix element vanishes for Bravais crystals, as well as for nonprimitive crystals in which every atom is at a center of inversion symmetry.

In second order the only contribution to $G_l(\mathbf{k}jj')$ of $O(\lambda^2)$ comes from the diagrams in Fig. 3. Its value is

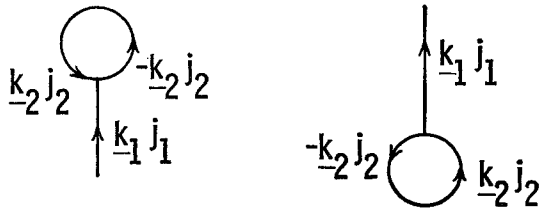

FIG. 4. Instantaneous phonons at three phonon vertices.

given by

$$G_l^{(2)}(\mathbf{k}jj') = 18\beta^2 \sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2} \sum_{l_1l_2} V^{(3)}(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2) \times V^{(3)}(\mathbf{k}j';-\mathbf{k}_1j_1;-\mathbf{k}_2j_2)a_{l_1}(\mathbf{k}_1j_1) \times a_{l_2}(\mathbf{k}_2j_2)\delta_{-l+l_1+l_2,0}. \quad (4.27)$$

The two diagrams shown in Figs. 3(a) and 3(b) are topologically equivalent, that is, one can be continuously deformed into the other. Their contributions to $G_l^{(2)}(\mathbf{k}jj')$ are equal, and according to rule 1 above it is necessary to calculate the contribution from only one of them and multiply it by two to take account of both contributions. We have drawn both diagrams only for illustrative purposes. In the present case the factor of 2 due to the occurrence of the two topologically equivalent diagrams cancels the factor of 1/2! which multiplies the second-order contributions to $G_l^{(2)}(\mathbf{k}jj')$.

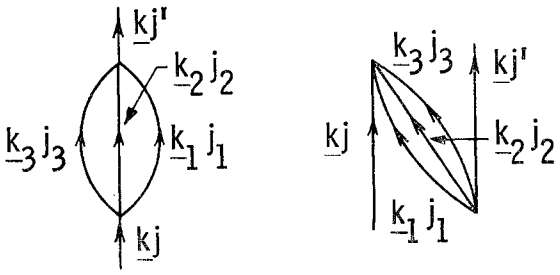

FIG. 5. Second-order diagrams which contribute to the proper self-energy to $O(\lambda^4)$.

[22] See, for example, R. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 37, second footnote. See also reference 21 for an explicit proof.

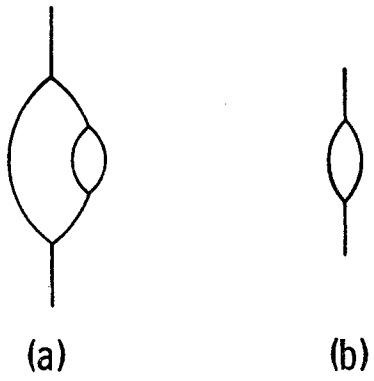

FIG. 6. (a) A fourth-order diagram containing a self-energy insertion which contributes to $G_l(\mathbf{k}jj')$. (b) The self-energy insertion which appears in Fig. 6(a).

The factor of 18 multiplying the sums in Eq. (4.27) arises from the fact that in Fig. 3(a) the phonon $(\mathbf{k}j)$ can pair with any of the three phonons at the lower vertex, while the phonon $(\mathbf{k}j')$ can pair with any of the three phonons at the upper vertex. The two remaining phonons at the lower vertex can pair with the two remaining phonons at the upper vertex in two ways. Each of these 18 pairing schemes contributes equally to $G_l^{(2)}(\mathbf{k}jj')$.

Equation (4.27) does not exhaust the contributions to $G_l^{(2)}(\mathbf{k}jj')$. There is a contribution associated with the diagrams in Fig. 5, but this is of fourth order in λ. Since we have retained only terms up to $O(\lambda^2)$ in the anharmonic Hamiltonian, we would not be consistent in including a contribution of $O(\lambda^4)$ in $G_l(\mathbf{k}jj')$.

Before proceeding to simplify Eqs. (4.26) and (4.27), we remark that we could carry out an additional simplification in the calculation of the phonon propagator $A_l(\mathbf{k}jj')$. This consists of replacing every free phonon propagator $a_l(\mathbf{k}j)$ in the expansion of $G_l(\mathbf{k}jj')$ by the corrected propagator $A_l(\mathbf{k}jj)$ and omitting all diagrams which contain self-energy insertions from the expansion. This procedure leads to an implicit equation for $G_l(\mathbf{k}jj')$ because the corrected propagators $A_l(\mathbf{k}jj)$ also contain $G_l(\mathbf{k}jj')$. This procedure would mean that a fourth-order diagram such as shown in Fig. 6(a) which would ordinarily be considered in calculating $G_l(\mathbf{k}jj')$ would now no longer be included since the right-hand line contains the self-energy insertion shown in Fig. 6(b). Such a procedure is very useful in various problems, but we will not make use of it in this discussion. Diagrams contributing to $G_l(\mathbf{k}jj')$ and containing no self-energy insertions are called *skeleton diagrams*.

We conclude this section by writing out more explicitly the contributions to $G_l(\mathbf{k}jj')$ given by Eqs. (4.26) and (4.27). If we refer back to Eqs. (4.12) and (4.14) we see that the sum over l_1 appearing in Eq. (4.26) is given by

$$\sum_{l=-\infty}^{\infty} a_l(\mathbf{k}j)=g_{\mathbf{k}j}(0)=2n(\mathbf{k}j)+1. \tag{4.28}$$

This result suggests that we supplement rule 2 above by adding to it the statement that with each bubble diagram fragment corresponding to an instantaneous phonon $(\mathbf{k}_i j_i)$ we associate a factor $[2n(\mathbf{k}_i j_i)+1]$. This rule applies equally well to instantaneous phonons at three phonon vertices in nonprimitive crystals in which every atom is not at a center of inversion symmetry.

With Eqs. (4.6) and (4.28) we can rewrite Eq. (4.26) as

$$G_l^{(1)}(\mathbf{k}jj')=-\frac{\beta\hbar^2}{8N}\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{[\omega(\mathbf{k}j)\omega(\mathbf{k}j')]^{1/2}\omega(\mathbf{k}_1j_1)}\times[2n(\mathbf{k}_1j_1)+1]. \tag{4.29}$$

We now make use of Eqs. (4.6) and (4.14) to rewrite Eq. (4.27) as

$$G_l^{(2)}(\mathbf{k}jj')=\frac{\beta^2\hbar^3}{16N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\sum_{l_1l_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)\Phi(\mathbf{k}j';-\mathbf{k}_1j_1;-\mathbf{k}_2j_2)}{[\omega(\mathbf{k}j)\omega(\mathbf{k}j')]^{1/2}\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\delta_{-l+l_1+l_2}\frac{2\omega(\mathbf{k}_1j_1)}{\beta\hbar}\frac{1}{\omega_{l_1}^2+\omega^2(\mathbf{k}_1j_1)}\frac{2\omega(\mathbf{k}_2j_2)}{\beta\hbar}\times\frac{1}{\omega_{l_2}^2+\omega^2(\mathbf{k}_2j_2)}. \tag{4.30}$$

We can eliminate the sum over l_2 with the aid of the δ-function restriction. The remaining sum over l_1 is readily evaluated by contour integration, with the result that

$$\sum_{l_1=-\infty}^{\infty}\frac{1}{\omega_{l_1}^2+\omega^2(\mathbf{k}_1j_1)}\frac{1}{(\omega_{l_1}-\omega_l)^2+\omega^2(\mathbf{k}_2j_2)}=\frac{\beta\hbar}{4\omega_1\omega_2}\left\{\frac{n_1+n_2+1}{i\omega_l+\omega_1+\omega_2}-\frac{n_1+n_2+1}{i\omega_l-\omega_1-\omega_2}+\frac{n_1-n_2}{i\omega_l-\omega_1+\omega_2}-\frac{n_1-n_2}{i\omega_l+\omega_1-\omega_2}\right\}, \tag{4.31}$$

where for simplicity we have put $\omega(\mathbf{k}_1j_1)=\omega_1$, etc. If we substitute this result into Eq. (4.30) we obtain finally

$$G_l^{(2)}(\mathbf{k}jj')=\frac{\beta\hbar^2}{16N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)\Phi(\mathbf{k}j';-\mathbf{k}_1j_1;-\mathbf{k}_2j_2)}{[\omega(\mathbf{k}j)\omega(\mathbf{k}j')]^{1/2}\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\left\{\frac{n_1+n_2+1}{i\omega_l+\omega_1+\omega_2}-\frac{n_1+n_2+1}{i\omega_l-\omega_1-\omega_2}+\frac{n_1-n_2}{i\omega_l-\omega_1+\omega_2}-\frac{n_1-n_2}{i\omega_l+\omega_1-\omega_2}\right\}. \tag{4.32}$$

From Eqs. (4.29) and (4.32), we see that $G_l(\mathbf{k}jj')$ is an intensive quantity as it must be.

V. RESULT FOR THE ONE-PHONON SCATTERING CROSS SECTION

From Eq. (3.17) we see that the correspondence between the discrete variable ω_l and the continuous variable ν is

$$i\omega_l \rightarrow \nu. \tag{5.1}$$

The function $a(\nu)$ can thus be written as

$$a(\nu)=\frac{\hbar}{2NM}\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\frac{1}{\beta\hbar}\left\{\frac{1}{\nu+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\nu)}+\frac{1}{-\nu+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\nu)}\right\}. \tag{5.2}$$

Combining this result with Eq. (3.25) we obtain for $B_{xy}(ll';\omega)$:

$$B_{xy}(ll';\omega)=\frac{1}{1-e^{-\beta\hbar\omega}}\frac{\hbar}{2NM}\times\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\frac{1}{2\pi i}\lim_{\delta\rightarrow 0+}\left\{\frac{1}{\omega+i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega+i\delta)}-\frac{1}{\omega-i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega-i\delta)}+\frac{1}{-\omega-i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega+i\delta)}-\frac{1}{-\omega+i\delta+\omega(\mathbf{k}j)-(1/\beta\hbar)G(\mathbf{k}j;\omega-i\delta)}\right\}. \tag{5.3}$$

From Eqs. (4.29) and (4.32) we find that

$$\lim_{\delta\rightarrow 0+}-\frac{1}{\beta\hbar}G(\mathbf{k}j;\omega\pm i\delta)=\Delta(\mathbf{k}j;\omega)\mp i\Gamma(\mathbf{k}j;\omega), \tag{5.4}$$

where

$$\Delta(\mathbf{k}j;\omega)=\frac{\hbar}{8N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega(\mathbf{k}_1j_1)}\times[2n(\mathbf{k}_1j_1)+1]+\frac{\hbar}{16N\omega(\mathbf{k}j)}\times\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\left\{-\frac{n_1+n_2+1}{(\omega+\omega_1+\omega_2)_P}+\frac{n_1+n_2+1}{(\omega-\omega_1-\omega_2)_P}-\frac{n_1-n_2}{(\omega-\omega_1+\omega_2)_P}+\frac{n_1-n_2}{(\omega+\omega_1-\omega_2)_P}\right\}, \tag{5.5a}$$

$$\Gamma(\mathbf{k}j;\omega)=\frac{\pi\hbar}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\times\{-(n_1+n_2+1)\delta(\omega+\omega_1+\omega_2)+(n_1+n_2+1)\delta(\omega-\omega_1-\omega_2)-(n_1-n_2)\delta(\omega-\omega_1+\omega_2)+(n_1-n_2)\delta(\omega+\omega_1-\omega_2)\}. \tag{5.5b}$$

With this result, $B_{xy}(ll';\omega)$ becomes

$$B_{xy}(ll';\omega)=\frac{1}{1-e^{-\beta\hbar\omega}}\frac{\hbar}{NM}\sum_{\mathbf{k},j}\frac{e_x(\mathbf{k}j)e_y(\mathbf{k}j)}{\omega(\mathbf{k}j)}e^{2\pi i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\times\left\{\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega+\omega(\mathbf{k}j)+\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\omega j;\omega)}+\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega-\omega(\mathbf{k}j)-\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}\right\}, \tag{5.6}$$

and we obtain finally that the one-phonon scattering cross section is given by

$$\frac{d^2\sigma_{\mathrm{coh}}{}^{(1)}}{d\Omega d\epsilon}=\frac{a^2}{\hbar}\frac{q_1}{q_0}S_1(\boldsymbol{\kappa},\omega)=\frac{N}{M}\frac{a^2}{2\pi}\frac{q_1}{q_0}\frac{e^{-2M}}{1-e^{-\beta\hbar\omega}}\sum_j\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega(\mathbf{k}j)}\times\left\{\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega-\omega(\mathbf{k}j)-\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}+\frac{\Gamma(\mathbf{k}j;\omega)}{[\omega+\omega(\mathbf{k}j)+\Delta(\mathbf{k}j;\omega)]^2+\Gamma^2(\mathbf{k}j;\omega)}\right\}, \tag{5.7}$$

where the vector $\mathbf{k}$ is related to the vector $\boldsymbol{\kappa}$ by

$$\boldsymbol{\kappa}=2\pi\mathbf{k}+2\pi\boldsymbol{\tau}. \tag{5.8}$$

The first term of this expression corresponds to processes in which the neutron gives up energy $\hbar\omega$ to the crystal, while the second term corresponds to

processes in which the neutron absorbs energy $\hbar\omega$ from the crystal.

We see that our result for the transition probability has a Lorentzian form, but with frequency-dependent widths and shifts. This latter circumstance means that if $\Delta(\mathbf{k}j;\omega)$ and $\Gamma(\mathbf{k}j;\omega)$ are not small compared with $\omega(\mathbf{k}j)$ the line shape given by Eq. (5.7) will be different from that described by a Lorentzian function.

If $\Delta(\mathbf{k}j;\omega)$ and $\Gamma(\mathbf{k}j;\omega)$ are small compared with $\omega(\mathbf{k}j)$, then we can approximate Eq. (5.7) as

$$\frac{d^2\sigma_{\rm coh}{}^{(1)}}{d\Omega d\epsilon}=\frac{N}{M}\frac{a^2}{2\pi}\frac{q_1}{q_0}e^{-2M}\sum_j\frac{[\boldsymbol{\kappa}\cdot\mathbf{e}(\mathbf{k}j)]^2}{\omega(\mathbf{k}j)}\times\Bigg\{\frac{1}{1-e^{-\beta\hbar\omega(\mathbf{k}j)}}\times\frac{\Gamma(\mathbf{k}j;\omega(\mathbf{k}j))}{[\omega-\omega(\mathbf{k}j)-\Delta(\mathbf{k}j;\omega(\mathbf{k}j))]^2+\Gamma^2(\mathbf{k}j;\omega(\mathbf{k}j))}+\frac{1}{e^{\beta\hbar\omega(\mathbf{k}j)}-1}\times\frac{\Gamma(\mathbf{k}j;\omega(\mathbf{k}j))}{[\omega+\omega(\mathbf{k}j)+\Delta(\mathbf{k}j;\omega(\mathbf{k}j))]^2+\Gamma^2(\mathbf{k}j;\omega(\mathbf{k}j))}\Bigg\}. \quad (5.9)$$

In writing this result, we have used the fact that $\Delta(\mathbf{k}j;\omega)$ is an even function of ω, while $\Gamma(\mathbf{k}j;\omega)$ is an odd function of ω. We see from this result that at the absolute zero of temperature only those scattering processes are possible in which the neutron excites a phonon. This is to be expected since a crystal in its ground state cannot give up a phonon to the neutron. In addition, since in the present approximation $\Gamma(\mathbf{k}j;\omega(\mathbf{k}j))$ is the imaginary part of the self-energy of the phonon $(\mathbf{k}j)$ and accordingly is the reciprocal of the lifetime of the phonon amplitude, we see from Eq. (5.9) that the width at half maximum of the peak in the energy distribution is the reciprocal of the phonon's lifetime.

The expressions for the phonon energy shift and width take simple forms in two limiting cases: the absolute zero of temperature, and the high-temperature limit. In the former case $n(\mathbf{k}j)=0$ and we obtain

$$\Delta(\mathbf{k}j;\omega)=\frac{\hbar}{8N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega(\mathbf{k}_1j_1)}+\frac{\hbar}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\Bigg\{\frac{1}{(\omega-\omega_1-\omega_2)_P}-\frac{1}{(\omega+\omega_1+\omega_2)_P}\Bigg\}, \quad (5.10a)$$

$$\Gamma(\mathbf{k}j;\omega)=\frac{\pi\hbar}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\{\delta(\omega-\omega_1-\omega_2)-\delta(\omega+\omega_1+\omega_2)\}. \quad (5.10b)$$

At high temperatures $n(\mathbf{k}j)\rightarrow kT/\hbar\omega(\mathbf{k}j)$, and we obtain

$$\Delta(\mathbf{k}j;\omega)=\frac{kT}{4N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega^2(\mathbf{k}_1j_1)}+\frac{kT}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\Bigg\{-\frac{\omega_1+\omega_2}{(\omega+\omega_1+\omega_2)_P}+\frac{\omega_1+\omega_2}{(\omega-\omega_1-\omega_2)_P}-\frac{\omega_1-\omega_2}{(\omega+\omega_1-\omega_2)_P}+\frac{\omega_1-\omega_2}{(\omega-\omega_1+\omega_2)_P}\Bigg\}, \quad (5.11a)$$

$$\Gamma(\mathbf{k}j;\omega)=\frac{\pi kT}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_1j_1)}\times\{-(\omega_1+\omega_2)\delta(\omega+\omega_1+\omega_2)+(\omega_1+\omega_2)\delta(\omega-\omega_1-\omega_2)-(\omega_1-\omega_2)\delta(\omega+\omega_1-\omega_2)+(\omega_1-\omega_2)\delta(\omega-\omega_1+\omega_2)\}. \quad (5.11b)$$

We note finally that in the approximation we have kept to in this paper, the quartic anharmonic terms contribute only to the frequency shift but not to the phonon lifetime. Moreover, both the cubic and quartic anharmonic contributions to $\Delta(\mathbf{k}j;\omega)$ are proportional to T at high temperatures.

Apart from differences in notation, the results we have presented in this section agree exactly with those obtained by Kokkedee.[6]

VI. PHONON SHIFTS AND WIDTHS FOR A SIMPLE MODEL OF A CRYSTAL

The expressions we have obtained in the preceding section are not without interest in themselves. However,

their full usefulness is not realized until they can be translated into numerical results which can be compared against experimental results.

In order to evaluate the expressions given by Eqs. (5.10) and (5.11) for a given solid, we have to make some assumptions about the nature of the forces acting between the atoms comprising the solid, that is, we have to adopt some model for the solid. This model must be sufficiently realistic that the results obtained through its use reflect, at least to some extent, the properties of the solid and not merely those of the model, and at the same time it should be simple enough that the already difficult numerical evaluation of the expressions in Eqs. (5.10) and (5.11) is not rendered intractable just because of the model adopted.

The model we have chosen to work with is a face-centered cubic lattice with central force interactions between pairs of atoms. The interatomic forces were assumed to be sufficiently short ranged, so that interactions between atoms which are more distant than nearest neighbors in the lattice could be neglected. As a model for a real solid, it probably describes the properties of the ideal rare gas solids (argon, krypton, etc.) most closely. However, it may also be used in a phenomenological treatment of the properties of metals.

This model has several features which make it an attractive choice as the basis for a preliminary attempt at the evaluation of the phonon width and shift. Firstly, it has been used in previous calculations of anharmonic properties of solids,[23] so that a computer program exists for the calculation of the normal mode frequencies $\{\omega(\mathbf{k}j)\}$ and the associated polarization vectors $\{e(\mathbf{k}j)\}$ for a large number of $\mathbf{k}$ values uniformly distributed throughout the first Brillouin zone of the crystal. Secondly, with this model the expressions in Eqs. (5.10) and (5.11) depend on the interactomic potential $\phi(r)$ only through the values of its second, third, and fourth derivatives evaluated at the separation between nearest-neighbor atoms in the crystal. For the present model, these parameters and the atomic mass can be factored outside the complicated sums over the $\mathbf{k}$'s and j's, which now become pure numbers independent of any assumptions about the analytic form of the interatomic potential function as a function of the interatomic separation. This means that the summations over the $\mathbf{k}$'s and j's need to be evaluated only once, and the resulting expressions for the phonon widths and shifts can then be used for any crystal for which our model is a reasonable approximation simply by substituting into them the values of the derivatives of the interatomic potential and the atomic mass appropriate to the crystal.

The first contribution to the shift in the phonon frequency we consider is the contribution due to the thermal expansion of the crystal. For the present model this shift, which we denote by $\Delta^{(0)}(\mathbf{k}j;\omega)$, is readily calculated. The normal mode frequencies $\omega(\mathbf{k}j)$ can be written for our model as[23]

$$\omega(\mathbf{k}j)=[2\phi''(r_0)/M]^{1/2}\lambda(\mathbf{k}j), \tag{6.1}$$

where $\lambda(\mathbf{k}j)$ is a dimensionless frequency which is independent of $\phi''(r_0)$ and M. In this expression r_0 is the value of the nearest-neighbor separation at temperature T. In reference 17 it is pointed out that a consistent treatment of thermal expansion effects in lattice dynamical problems is greatly simplified if the thermal properties of a crystal are expanded about the values they have in the lattice configuration which corresponds to the minimum of the *potential energy*. If the nearest-neighbor separation corresponding to the minimum of the potential energy is denoted by $\bar{r}_0$, then we can write

$$r_0=(1+\epsilon)\bar{r}_0, \tag{6.2}$$

where ϵ is called the linear expansivity.

If we substitute Eq. (6.2) into Eq. (6.1) and expand the result in powers of ϵ, we find that to lowest order in ϵ

$$\omega(\mathbf{k}j)=\left(\frac{2\phi''(\bar{r}_0)}{M}\right)^{1/2}\lambda(\mathbf{k}j) + \frac{1}{2}\left(\frac{2\phi''(\bar{r}_0)}{M}\right)^{1/2}\epsilon\bar{r}_0\frac{\phi'''(\bar{r}_0)}{\phi''(\bar{r}_0)}\lambda(\mathbf{k}j). \tag{6.3}$$

We consequently have that

$$\Delta^{(0)}(\mathbf{k}j;\omega)=\frac{1}{2}\left(\frac{2\phi''(\bar{r}_0)}{M}\right)^{1/2}\epsilon\bar{r}_0\frac{\phi'''(\bar{r}_0)}{\phi''(\bar{r}_0)}\lambda(\mathbf{k}j). \tag{6.4}$$

In reference 17 the expansivity ϵ was found to have the following forms at the absolute zero of temperature, and at high temperatures, respectively,

$$\epsilon \underset{0^\circ\mathrm{K}}{=} -\frac{\bar{\epsilon}_0}{12\bar{r}_0}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}, \tag{6.5a}$$

$$\epsilon \underset{T\to\infty}{=} -\frac{kT}{4\bar{r}_0}\frac{\phi'''(\bar{r}_0)}{[\phi''(\bar{r}_0)]^2}. \tag{6.5b}$$

In Eq. (6.5a) $\bar{\epsilon}_0$ is the zero-point energy per atom in the configuration which corresponds to the minimum of the potential energy. It is given by[24]

$$\bar{\epsilon}_0=1.0227\hbar[8\phi''(\bar{r}_0)/M]^{1/2}. \tag{6.6}$$

That ϵ does not vanish at the absolute zero of temperature is a manifestation of the fact that the equilibrium value of the nearest-neighbor separation at any temperature corresponds to the minimum of the Helmholtz

[23] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (New York) **15**, 360 (1961).

[24] C. Domb and C. Isenberg (private communication). We would like to thank these authors for communicating this result to us.

free energy, and at absolute zero this is the sum of the potential and zero-point energies.

Combining Eqs. (6.4) and (6.5) we can express $\Delta^{(0)}(\mathbf{k}j;\omega)$ as

$$\frac{\Delta^{(0)}(kj;\omega)}{\omega_L} \underset{0°\mathrm{K}}{=} -\frac{\hbar}{48}\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^3}\lambda(\mathbf{k}j), \quad (6.7a)$$

$$\frac{\Delta^{(0)}(\mathbf{k}j;\omega)}{\omega_L} \underset{T\to\infty}{=} -\frac{kT}{16}\frac{[\phi'''(\bar{r}_0)]^2}{[\phi''(\bar{r}_0)]^3}\lambda(\mathbf{k}j), \quad (6.7b)$$

where $\omega_L=[8\phi''(\bar{r}_0)/M]^{1/2}$ is the maximum frequency of the crystal in the harmonic approximation. We note that $\Delta^{(0)}(\mathbf{k}j;\omega)$ is independent of the energy parameter ω.

In all that follows, it is to be understood that all derivatives of the potential energy which appear in our analysis are to be evaluated in the configuration which corresponds to the minimum of the potential energy. It is not necessary to make corrections for the effects of thermal expansion in the purely anharmonic contributions to $\Delta(\mathbf{k}j;\omega)$ and $\Gamma(\mathbf{k}j;\omega)$ since these are of higher order in λ than we have chosen to consider. For typographical convenience we omit the bar over r_0 in the equations that follow.

We now turn to the quartic anharmonic contribution to the phonon frequency shift. If we use the results of reference 23 we can greatly simplify the evaluation of the quartic anharmonic contribution to $G_e(\mathbf{k}jj')$ both at the absolute zero of temperature and at high temperatures. In particular, for special directions of the wave vector $\mathbf{k}$ it is possible to evaluate the expressions in closed form.

In the high-temperature limit we require the sum

$$S(\mathbf{k}jj')=\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega^2(\mathbf{k}_1j_1)}. \quad (6.8)$$

The coefficient $\Phi(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1)$ is given for the present model by

$$\Phi(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1)$$
$$=\frac{2\phi''''(r_0)}{M^2}\sum_{\mathrm{n,n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]$$
$$\times[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n})$$
$$\times\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}). \quad (6.9)$$

The vector $\mathbf{n}$ is a dimensionless vector with integer components which is defined by

$$\mathbf{x}(l)=\tfrac{1}{2}a_0(n_x,n_y,n_z), \quad (6.10)$$

where n_x, n_y, n_z are three integers which are all even or all odd. a_0 is the lattice parameter and the sum over $\mathbf{n}$ runs over the twelve nearest neighbors to a given atom.

The sum $S(\mathbf{k}jj')$ then takes the form

$$S(\mathbf{k}jj')=\frac{2\phi''''(r_0)}{M^2}$$
$$\times\sum_{\mathrm{n,n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n})$$
$$\times\sum_{\mathbf{k}_1,j_1}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2}{\omega^2(\mathbf{k}_1j_1)}\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}). \quad (6.11)$$

The sum over $\mathbf{k}_1$ and j_1 has been shown to be independent of $\mathbf{n}$ in reference 23 and has the value

$$\sum_{\mathbf{k}_1,j_1}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2}{\omega^2(\mathbf{k}_1j_1)}\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n})=\frac{NM}{4\phi''(r_0)}. \quad (6.12)$$

If we substitute this result into Eq. (6.11) we find that

$$S(\mathbf{k}jj')=\frac{N}{2M}\frac{\phi''''(r_0)}{\phi''(r_0)}\sum_{\mathrm{n,n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]$$
$$\times\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}). \quad (6.13)$$

We thus have the result that

$$-\frac{1}{\beta\hbar}G^{(1)}(\mathbf{k}jj')=\frac{kT}{8M}\frac{\phi''''(r_0)}{\phi''(r_0)}\frac{1}{[\omega(\mathbf{k}j)\omega(\mathbf{k}j')]^{1/2}}$$
$$\times\sum_{\mathrm{n}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n}). \quad (6.14)$$

At the absolute zero of temperature the sum we have to evaluate is

$$T(\mathbf{k}jj')=\sum_{\mathbf{k}_1,j_1}\frac{\Phi(-\mathbf{k}j;\mathbf{k}j';\mathbf{k}_1j_1;-\mathbf{k}_1j_1)}{\omega(\mathbf{k}_1j_1)} \quad (6.15)$$
$$=\frac{2\phi''''(r_0)}{M^2}\sum_{\mathrm{n,n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]$$
$$\times\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n})\sum_{\mathbf{k}_1,j_1}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2}{\omega(\mathbf{k}_1j_1)}$$
$$\times\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}). \quad (6.16)$$

The sum over $\mathbf{k}_1$ and j_1 is shown to be independent of $\mathbf{n}$ in reference 23 and has the value

$$\sum_{\mathbf{k}_1,j_1}\frac{[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)]^2}{\omega(\mathbf{k}_1j_1)}\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n})=\frac{M}{6\hbar}\frac{N\epsilon_0}{\phi''(r_0)}. \quad (6.17)$$

With this result Eq. (6.16) becomes

$$T(\mathbf{k}jj')=\frac{N}{3\hbar M}\frac{\phi''''(r_0)}{\phi''(r_0)}\sum_{\mathrm{n,n.n.}}[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)]$$
$$\times[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n}), \quad (6.18)$$

and we obtain finally

$$-\frac{1}{\beta\hbar}G^{(1)}(\mathbf{k}jj') \underset{0^\circ\mathrm{K}}{=} \frac{\epsilon_0}{24M}\frac{\phi''''(r_0)}{\phi''(r_0)}\frac{1}{[\omega(\mathbf{k}j)\omega(\mathbf{k}j')^{1/2}]} \times \sum_{\mathrm{n,n.n.}} [\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j')]\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n}). \quad (6.19)$$

To proceed analytically past this point we must know the eigenvectors and eigenvalues of the dynamical matrix explicitly. This is not possible in general. However, as long as we are interested only in the quartic contribution to the frequency shift $\Delta^{(1)}(\mathbf{k}j;\omega)$ we require only the diagonal elements of $-(1/\beta\hbar)G(\mathbf{k}jj')$. In this case we can carry out the remaining calculations in closed form. It follows almost trivially from the results of reference 23 that

$$\sum_{\mathrm{n,n.n.}} [\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)]^2\sin^2(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n}) = 2\lambda^2(\mathbf{k}j), \quad (6.20)$$

where $\lambda(\mathbf{k}j)$ has been defined in Eq. (6.1).

We thus obtain the results that

$$\frac{\Delta^{(1)}(\mathbf{k}j;\omega)}{\omega_L} \underset{T\to\infty}{=} \frac{kT}{16}\frac{\phi''''(r_0)}{[\phi''(r_0)]^2}\lambda(\mathbf{k}j) \quad (6.21a)$$

$$\underset{0^\circ\mathrm{K}}{=} \frac{\epsilon_0}{48}\frac{\phi''''(r_0)}{[\phi''(r_0)]^2}\lambda(\mathbf{k}j). \quad (6.21b)$$

To complete our analysis of the thermal expansion and quartic anharmonic contributions to the phonon frequency shift, we present here the expressions for $\lambda(\mathbf{k}j)$ obtained for our model for $\mathbf{k}$ vectors lying along the high-symmetry directions in cubic crystals.[23]

[100] direction: $k_x=k$, $k_y=k_y=0$

$$\lambda(\mathbf{k}1)=2\sin(\pi a_0k/2), \quad (6.22a)$$

$$\lambda(\mathbf{k}2)=\lambda(\mathbf{k}3)=\sqrt{2}\sin(\pi a_0k/2). \quad (6.22b)$$

[110] direction: $k_x=k_y=k/\sqrt{2}$, $k_z=0$

$$\lambda(\mathbf{k}1)=[2\sin^2(\pi a_0k/2\sqrt{2})+2\sin^2(\pi a_0k/\sqrt{2})]^{1/2}, \quad (6.23a)$$

$$\lambda(\mathbf{k}2)=2\sin(\pi a_0k/2\sqrt{2}), \quad (6.23b)$$

$$\lambda(\mathbf{k}3)=\sqrt{2}\sin(\pi a_0k/2\sqrt{2}). \quad (6.23c)$$

[111] direction: $k_x=k_y=k_z=k/\sqrt{3}$

$$\lambda(\mathbf{k}1)=2\sin(\pi a_0k/\sqrt{3}), \quad (6.24a)$$

$$\lambda(\mathbf{k}2)=\lambda(\mathbf{k}3)=\sin(\pi a_0k/\sqrt{3}). \quad (6.24b)$$

We come finally to a discussion of the cubic anharmonic contribution to $\Delta(\mathbf{k}j;\omega)$ and $\Gamma(\mathbf{k}j;\omega)$. In our numerical calculations we have dealt with the high-temperature forms of these expressions only, because the phonon shifts and widths are expected to be larger at high temperatures than at low, and because experimental results for these quantities are available in this limit. However, for the sake of completeness and for future references we present the expressions obtained for our model for the case of zero temperature as well.

For the simple lattice model we are using in the present calculations the coefficient $\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)$ is[23]

$$\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2) = -(2i)^3\frac{\phi'''(r_0)}{2(2M)^{3/2}} \times F(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2), \quad (6.25)$$

where $F(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)$ is a real coefficient which is given by

$$F(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2) = \sum_{\mathrm{n,n.n.}} \exp(\tfrac{1}{2}\pi i a_0\mathbf{n}\cdot\boldsymbol{\tau})[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}j)][\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_1j_1)] \times[\mathbf{n}\cdot\mathbf{e}(\mathbf{k}_2j_2)]\sin(\tfrac{1}{2}\pi a_0\mathbf{k}\cdot\mathbf{n})\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_1\cdot\mathbf{n}) \times\sin(\tfrac{1}{2}\pi a_0\mathbf{k}_2\cdot\mathbf{n}). \quad (6.26)$$

In this expression $\boldsymbol{\tau}$ is the translation vector of the reciprocal lattice which satisfies $-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2=\boldsymbol{\tau}$.

If we substitute Eq. (6.25) into Eqs. (5.10) we obtain the results that at the absolute zero of temperature

$$\frac{\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L} = \frac{\hbar\omega_L}{256\lambda(\mathbf{k}j)}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^3}\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2) \times\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda(\mathbf{k}_1j_1)\lambda(\mathbf{k}_2j_2)}\left\{\frac{1}{(\lambda-\lambda_1-\lambda_2)_P} - \frac{1}{(\lambda+\lambda_1+\lambda_2)_P}\right\}, \quad (6.27a)$$

$$\frac{\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L} = \frac{\pi\hbar\omega_L}{256\lambda(\mathbf{k}j)}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^3}\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2) \times\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda(\mathbf{k}_1j_1)\lambda(\mathbf{k}_2j_2)}\delta(\lambda-\lambda_1-\lambda_2). \quad (6.27b)$$

In the high-temperature limit we can write the cubic anharmonic contributions to $\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))$ and $\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))$ compactly as

$$\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j)) = -\frac{kT}{16N\omega(\mathbf{k}j)}\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2) \times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)} \times\frac{\omega(\mathbf{k}_1j_1)+\omega(\mathbf{k}_2j_2)}{[\omega(\mathbf{k}j)+\omega(\mathbf{k}_1j_1)+\omega(\mathbf{k}_2j_2)]_P}, \quad (6.28a)$$

$$\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))$$
$$=\frac{\pi kT}{16N}\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{|\Phi(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)|^2}{\omega^2(\mathbf{k}_1j_1)\omega^2(\mathbf{k}_2j_2)}\times\delta(\omega(\mathbf{k}j)+\omega(\mathbf{k}_1j_1)+\omega(\mathbf{k}_2j_2)),\quad(6.28b)$$

where we have now adopted the convention that

$$\omega(\mathbf{k}-j)=-\omega(\mathbf{k}j).\quad(6.29)$$

The Φ coefficients are unaffected by the replacement of any of the branch indices by their negatives.

If we substitute Eq. (6.25) into Eqs. (6.28) we obtain finally

$$\frac{\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}$$
$$=-\frac{kT}{128}\frac{1}{\lambda(\mathbf{k}j)}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^3}\frac{1}{N}\times\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)}\times\frac{\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_2j_2)}{[\lambda(\mathbf{k}j)+\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_1j_1)]_P},\quad(6.30a)$$

$$\frac{\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}$$
$$=\frac{\pi kT}{128}\frac{[\phi'''(r_0)]^2}{[\phi''(r_0)]^3}\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)}\times\delta(\lambda(\mathbf{k}j)+\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_2j_2)).\quad(6.30b)$$

These expressions provided the starting point for our numerical calculations.

VII. NUMERICAL RESULTS

In the present work it was decided to use our model to approximate lead. This choice was made primarily because recently measurements of the phonon widths in lead have been made by Brockhouse and co-workers.[1] Their measurements were carried out at 425°K, which is more than four times the Debye characteristic temperature for lead. Thus, our high-temperature results should be valid in this case.

It should be emphasized that our decision to approximate lead by our simple model was not due to any belief that it is a good approximation for lead. If anything, it is an inadequate model for lead. Measurements by Brockhouse *et al.*[10] indicate that the range of the interatomic forces in lead extends out to at least fifth nearest neighbors, and the interatomic forces are certainly not of the central force type. Nevertheless, despite the known deficiencies of our model as a representation for lead, the availability of experimental data, the philosophy that almost any model is better than no model at all, and the desire to see how closely, if at all, theory can match experiment, prompted us to make the present comparisons.

The values of the derivatives of the interatomic potential which are required to translate our formal results into numerical results have been obtained in reference 17. Since the manner in which these values were extracted from experimental data on the thermal expansion, compressibility, and lattice parameter of lead has been discussed in some detail in this reference, we will not repeat the discussion here, and simply quote the results:

$$\begin{aligned}\bar{r}_0&=3.472\times10^{-8}\text{ cm},\\ \phi''(\bar{r}_0)&=1.819\times10^{4}\text{ erg/cm}^2,\\ \phi'''(\bar{r}_0)&=-9.693\times10^{12}\text{ erg/cm}^3,\\ \phi''''(\bar{r}_0)&=4.016\times10^{21}\text{ erg/cm}^4.\end{aligned}\quad(7.1)$$

In expressing the high-temperature results it is convenient to introduce the characteristic temperature Θ_∞ which is defined by[25]

$$\Theta_\infty=\frac{\hbar}{k}\left(\frac{5}{3}\mu_2\right)^{1/2}\quad(7.2)$$

where μ_2 is the second moment of the frequency spectrum of the harmonic crystal. In the present case

$$\mu_2=4\phi''(\bar{r}_0)/M.\quad(7.3)$$

Θ_∞ defined by Eq. (7.2) is the limiting high-temperature value of the equivalent Debye characteristic temperature. Its value calculated with the results of Eq. (7.1) is

$$\Theta_\infty=143.4^\circ\text{K}.\quad(7.4)$$

This value is rather higher than the value of ~105°K calculated by Horton and Schiff,[26] and gives some idea of the internal consistency of our model for lead.

We also quote the values of ω_L and $\epsilon_0=1.0227\hbar\omega_L$ obtained for our model:

$$\omega_L=2.057\times10^{13}\text{ sec}^{-1},\quad(7.5a)$$

$$\epsilon_0=2.218\times10^{-14}\text{ erg}.\quad(7.5b)$$

[25] C. Domb and L. Salter, Phil. Mag. **43**, 1083 (1952).
[26] G. K. Horton and H. Schiff, Proc. Roy. Soc. (London) **A250**, 248 (1959).

We can now summarize the results for our model as follows. At 0°K we have

$$\frac{\Delta^{(0)}(\mathbf{k}j;\omega)}{\omega_L}=-0.007209\lambda(\mathbf{k}j), \tag{7.6a}$$

$$\frac{\Delta^{(1)}(\mathbf{k}j;\omega)}{\omega_L}=0.005606\lambda(\mathbf{k}j), \tag{7.6b}$$

$$\frac{\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}=\frac{0.001322}{\lambda(\mathbf{k}j)}\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda(\mathbf{k}_1j_1)\lambda(\mathbf{k}_2j_2)}$$
$$\times\left\{\frac{1}{[\lambda(\mathbf{k}j)-\lambda(\mathbf{k}_1j_1)-\lambda(\mathbf{k}_2j_2)]_P}-\frac{1}{[\lambda(\mathbf{k}j)+\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_2j_2)]_P}\right\}, \tag{7.6c}$$

$$\frac{\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}=\frac{0.004152}{\lambda(\mathbf{k}j)}\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,j_1j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda(\mathbf{k}_1j_1)\lambda(\mathbf{k}_2j_2)}\delta(\lambda(\mathbf{k}j)-\lambda(\mathbf{k}_1j_1)-\lambda(\mathbf{k}_2j_2)). \tag{7.6d}$$

At high temperatures we find

$$\frac{\Delta^{(0)}(\mathbf{k}j;\omega)}{\omega_L}=-(0.01930)\left(\frac{T}{\Theta_\infty}\right)\lambda(\mathbf{k}j), \tag{7.7a}$$

$$\frac{\Delta^{(1)}(\mathbf{k}j;\omega)}{\omega_L}=(0.01501)\left(\frac{T}{\Theta_\infty}\right)\lambda(\mathbf{k}j), \tag{7.7b}$$

$$\frac{\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}=-\frac{0.002413}{\lambda(\mathbf{k}j)}\left(\frac{T}{\Theta_\infty}\right)\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)}$$
$$\times\frac{\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_2j_2)}{[\lambda(kj)+\lambda(k_1j_1)+\lambda(k_2j_2)]_P}, \tag{7.7c}$$

$$\frac{\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))}{\omega_L}=(0.007581)\left(\frac{T}{\Theta_\infty}\right)\frac{1}{N}\sum_{\mathbf{k}_1\mathbf{k}_2,\pm j_1\pm j_2}\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{F^2(-\mathbf{k}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2)}{\lambda^2(\mathbf{k}_1j_1)\lambda^2(\mathbf{k}_2j_2)}$$
$$\times\delta(\lambda(\mathbf{k}j)+\lambda(\mathbf{k}_1j_1)+\lambda(\mathbf{k}_2j_2)). \tag{7.7d}$$

The numerical evaluation of $\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L$ and $\Gamma^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L$ was carried out on an IBM 7090 computer in the following manner. Values for the wave vector $\mathbf{k}$ and polarization index j were chosen and were then fed into the computer as input data. The computer then selected a value of $\mathbf{k}_1$ in a systematic way. It then formed the vector $\mathbf{k}-\mathbf{k}_1$ and checked to see if it lay inside the first Brillouin zone or not. If it did it was called $\mathbf{k}_2$, and the summand was evaluated for these values of the wave vectors and then summed over the polarization indices j_1 and j_2. Such a contribution to the sums was called a *normal contribution*. If the vector $\mathbf{k}-\mathbf{k}_1$ lay outside the first Brillouin zone the computer determined the unique translation vector of the reciprocal lattice, $\boldsymbol{\tau}$, which translated this vector back inside the first zone. The vector $\boldsymbol{\tau}+\mathbf{k}-\mathbf{k}_1$ was then called $\mathbf{k}_2$ and the calculation proceeded as in the normal case. Such contributions to the sums were called *umklapp contributions*. The computer then selected a new value of $\mathbf{k}_1$ and the cycle was repeated. The normal and umklapp contributions to the phonon shift and width for each choice of $\mathbf{k}$ and j were tabulated separately together with their sum, so that the relative importance of the normal and umklapp contributions to these quantities could be studied.

The principal difficulty encountered in these calculations was finding a suitable representation for the Dirac δ function and the Cauchy principal value which appear in Eqs. (7.7c) and (7.7d). The first calculations were carried out using the representations

$$\delta(x)=\lim_{T\to\infty}\frac{\sin xT}{\pi x},\quad \left(\frac{1}{x}\right)_P=\lim_{T\to\infty}\frac{1-\cos xT}{x}, \tag{7.8}$$

for finite but large values of T. However, it was found that as T was varied the results obtained showed an oscillatory behavior and did not seem to be approaching a well-defined limit as T was increased. The number of

$\mathbf{k}_1$ values used in these calculations was 2048 in the entire zone.

The number of $\mathbf{k}_1$ values was increased to 6912, and different representations for the δ function and principal value were used:

$$\delta(x)=\lim_{\epsilon\to 0+}\frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2},\quad \left(\frac{1}{x}\right)_P=\lim_{\epsilon\to 0+}\frac{x}{x^2+\epsilon^2}, \tag{7.9}$$

where ϵ was chosen to be small but finite. The results in this case displayed a monotone behavior with decreasing ϵ until ϵ got very small whereupon the results behaved in an unpredictable way. The origin of these effects lies in the fact that in order that Eqs. (7.9) represent adequate approximations to the desired functions ϵ must be small. At the same time, it cannot be smaller than the smallest increment in x which results from our use of a finite number of $\mathbf{k}$ values in carrying out the sums over $\mathbf{k}_1$ and $\mathbf{k}_2$. The optimum value of ϵ for a given number of $\mathbf{k}$ values seems to depend on the values of $\mathbf{k}$ and j for which the calculation is being carried out, and could only be determined by trial and error, making this method a rather costly one. However, in some cases, it was possible to carry out the extrapolation to $\epsilon=0$.

In Fig. 7 we show the results obtained in this way, but using a fixed small value of ϵ, $\epsilon=10^{-3}$, for the phonon widths for longitudinal and transverse phonons propagating in the [100] direction in $\mathbf{k}$ space. The theoretical results are compared against the experimental results of Brockhouse, *et al.*[10] Although there is order of magnitude agreement between the two sets of results it cannot be said at the present time whether the discrepancies are due to our use of a rather simple model to describe lead, or are simply a reflection of the errors introduced by our computational techniques in dealing with the δ function. Accordingly, the present numerical results must be regarded as quite preliminary.

Yet a third method was employed in dealing with the δ function appearing in the expression for the phonon width. This method consisted of replacing the vector $\mathbf{k}_2$ in the sum by its equivalent $\boldsymbol{\tau}+\mathbf{k}-\mathbf{k}_1$. Since $\omega(\mathbf{k}j)$ is a periodic function of $\mathbf{k}$ with its periods defined by

$$\omega(\mathbf{k}j)=\omega(\mathbf{k}+\boldsymbol{\tau}j), \tag{7.10}$$

where $\boldsymbol{\tau}$ is an arbitrary translation vector of the reciprocal lattice, and since it is also an even function of $\mathbf{k}$, the argument of the δ function can be written as $\omega(\mathbf{k}j)+\omega(\mathbf{k}_1j_1)+\omega(\mathbf{k}-\mathbf{k}_1j_2)$. Since $\mathbf{k}$ and j are fixed, this expression is a function of $\mathbf{k}_1$ only, for fixed j_1 and j_2.

A program was written for the computer for solving the equation

$$\omega(\mathbf{k}j)+\omega(\mathbf{k}_1j_1)+\omega(\mathbf{k}-\mathbf{k}_1j_2)=0, \tag{7.11}$$

subject to the condition that $\boldsymbol{\tau}+\mathbf{k}-\mathbf{k}_1$ lie inside the first Brillouin zone (recall that j_1 and j_2 can assume both positive and negative values). The summation over $\mathbf{k}_1$ was then carried out over the two-dimensional surface in $\mathbf{k}_1$ space defined by Eq. (7.11), allowance being made for the density of transition frequencies introduced by this method of handling the δ function. The surface in $\mathbf{k}_1$ space generated in this way for a given $\mathbf{k}$ and fixed j, j_1, and j_2 was in agreement with the results of such general statements as can be made about the shapes of surfaces obtained in this way.[27] However, as a method for evaluating the phonon widths, it proved to be far too lengthy for the computer available, and was soon abandoned.

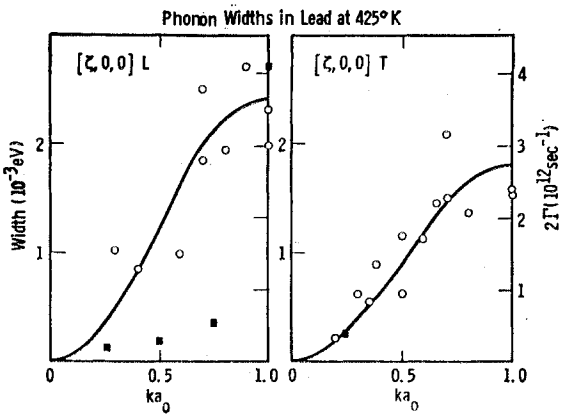

FIG. 7. Comparison between theoretical and experimental results for 2Γ, the width at half maximum of the peaks in the energy distribution of neutrons scattered by longitudinal and transverse lattice waves propagating in the [100] direction in lead. ○, experimental points determined by Brockhouse *et al.* (reference 10). ■, the results of the present calculations. The solid line is the best fit of the experimental data by a function of the form $\sin^2(\pi ka_0/2)$.

Of the high-temperature results we computed for $\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))$ we quote only two. These are the values for transverse phonons propagating in the [100] direction for values of ka_0 equal to 0.25 and 0.50. The results are

$ka_0=0.25$:

$$\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L=-(0.00306)(T/\Theta_\infty), \tag{7.12a}$$

$ka_0=0.50$:

$$\Delta^{(2)}(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L=-(0.00330)(T/\Theta_\infty). \tag{7.12b}$$

If we combine these values with the values of the shifts due to thermal expansion and four-phonon processes, which are computed from Eqs. (7.7a) ,(7.7b), and (6.22b), we obtain finally:

$ka_0=0.25$:

$$\Delta(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L=-(0.00538)(T/\Theta_\infty), \tag{7.13a}$$

$ka_0=0.50$:

$$\Delta(\mathbf{k}j;\omega(\mathbf{k}j))/\omega_L=-(0.00759)(T/\Theta_\infty). \tag{7.13b}$$

[27] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), Chap. III.

VIII. DISCUSSION

In summary, we have presented in this paper a theoretical and numerical study of the one-phonon differential scattering cross section for the coherent scattering of neutrons by an anharmonic Bravais crystal. It is hoped that the theoretical analysis contained in this paper presents clearly the nature of the approximations made in this and in previous investigations of this problem.

From the purely theoretical standpoint, there is one problem which remains to be treated in a more satisfactory manner than was done in this paper. This is the determination of the shift in the phonon frequency due to thermal expansion. In this paper we have used an approximate method to make this correction. We have calculated the normal mode frequencies in the strict harmonic approximation and have then expanded the lattice and have determined how the frequencies change. The correct procedure is to expand the lattice first and to compute the frequencies of the expanded lattice. This can easily be done formally using perturbation theory.[21] The same procedure must be employed in determining the linear expansivity. We have computed the free energy in the strict harmonic approximation and have minimized this with respect to variations of ϵ. In fact, the free energy must be computed for the deformed crystal and the value of ϵ as a function of temperature determined by minimizing the free energy of the deformed crystal with respect to ϵ. Formal expressions for ϵ obtained in this way exist.[21,28] If the result for ϵ is combined with the expression for the change in $\omega(\mathbf{k}j)$ due to arbitrary strains, we obtain the phonon frequency shift due to thermal expansion. Such a calculation has recently been carried out, and will be described elsewhere. The result of this calculation which is relevant here is that although we have used an approximate method to obtain $\Delta^{(0)}\omega(\mathbf{k}j)$, the result is nevertheless correct for the model with which we work. It is important to know these shifts accurately because the experimentally observed shifts include both these shifts and the shifts due to the three- and four-phonon processes. To study the latter we have to know the former. We hope to report on accurate calculations of these shifts in a subsequent paper in this series.

From the computational standpoint, there is much yet to be done in developing techniques for the evaluation of the expressions for the phonon widths and shifts due to three- and four-phonon processes. If we seriously hope to reproduce or predict experimental results we must work with more realistic (=more complicated) crystal models than we have used in our calculations. This, in turn, means that the computational difficulties will increase, and such calculations will probably remain impractical to carry out unless more effective computational techniques are developed.

In view of the importance of calculations of the phonon widths and shifts for several different problems in solid-state physics, investigations into possible new methods for carrying out such calculations are continuing. Recently a method has been devised for the evaluation of phonon widths and shifts which does not require the explicit utilization of the δ-function and principal-value restrictions which appear in Eqs. (7.7c) and (7.7d). A description of this method will be given in another paper.

The prime goal of theoretical work on the scattering of neutrons by anharmonic crystals at the present time would appear to be the reproduction of experimental results for the phonon widths and shifts. Eventually, when both experimental and theoretical results improve it should be possible to use the experimental results to obtain information about the anharmonic forces in solids.

[28] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.

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