

an iron ion of approximately twice its mass while the associated state corresponds to replacing two  $\text{Na}^+$  ions by an iron ion of about the same mass as the two ions it replaces. A quantitative estimate of the magnitude of these two effects will require a detailed theoretical treatment of the problem, which has not yet been attempted. The magnitude of the effect is so great, however, that even a crude calculation may be useful. It is interesting that the data on precipitated  $\text{CoCl}_2$  indicate a temperature dependence of  $f$  which is between that found for the two cases considered here (see I).

The broad linewidth observed for the isolated iron ions ( $\sim 1$  mm/sec) may be the result of quadrupole broadening from a Jahn-Teller type distortion or a trapped hole in the vicinity of the iron ion, although no noticeable narrowing was observed as the temperature was raised.

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## Neutron Scattering by an Anharmonic Crystal\*

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Baym's treatment of coherent scattering of slow neutrons by a crystal is examined and modified to include effects due to the cubic-anharmonic term in the lattice potential to second order in the coupling constant. Corrections to the Debye-Waller factor and to the "one-phonon" resonance peak are obtained, which appear to be negligible ( $\approx 0.01\%$ ) for the case of a Bravais lattice and certainly  $< 1\%$  in other cases.

### I. INTRODUCTION

WE would like to derive an expression for the coherent scattering cross section for slow neutrons, in which the anharmonic terms in the lattice potential are taken into consideration. Much work has been done on the problem of scattering from a perfect (harmonic) crystal,<sup>1-3</sup> where it is found that the coherent part may be written as a sum of terms representing scattering with absorption or emission of a number of phonons. The elastic term gives rise to peaks in the energy spectrum of the scattered neutrons (diffraction pattern) at the Bragg angles and the one-phonon term in the expression also gives rise to a  $\delta$ -function peak at the phonon energy. It has been tacitly assumed that for a nonperfect crystal the one-phonon peak becomes broadened by the interactions into a Lorentzian shape whose width is the inverse of the phonon lifetime. Such lifetime effects may be described in terms of the phonon Green's function and it is the purpose of this study to see to what extent the singular features of the cross section are related to the Green's function.

The contribution from scattering with multiple phonon emission or absorption produces a continuous

background in the harmonic case and, by continuity arguments, also in the weakly coupled case.

Experiments by Brockhouse *et al.*<sup>4</sup> have measured large widths in scattering from lead at high temperatures and some doubt has surrounded the form of the Debye-Waller factor. Although I have been unable quantitatively to explain these large widths (the theory, in any case, has treated the anharmonic nonmetallic crystal) the form of the result shows that for temperatures where such anharmonicities are considerable, one should expect a departure from the simple Lorentzian shape. This statement is very tentative because we have assumed weak coupling, working to second order in the coupling constant in a consistent manner.

The problem has been discussed by Brout,<sup>5</sup> Baym,<sup>6</sup> Krivoglaz,<sup>7</sup> and Maradudin.<sup>8</sup> Brout gives a general discussion of the energy spectrum of particles scattered from a system in terms of the widths and shifts of the states of that system. The approach of the other authors is a direct investigation of the formula for the coherent cross section. The present work follows on from Baym's analysis. We show that his result is applicable to a crystal with harmonic forces (including impurities and vacancies) but that it needs modification before being applied to the anharmonic case.

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<sup>1</sup> G. Placzek and L. Van Hove, *Phys. Rev.* **93**, 1207 (1954).

<sup>2</sup> A. C. Zemach and R. J. Glauber, *Phys. Rev.* **101**, 118 (1956).

<sup>3</sup> L. S. Kothari and K. S. Singwi, *Proc. Roy. Soc. (London)* **A231**, 293 (1955).

<sup>4</sup> B. N. Brockhouse, T. Arase, C. Caglioti, K. R. Rao, and A. D. B. Woods, *Phys. Rev.* **128**, 1099 (1962).

<sup>5</sup> R. Brout, *Phys. Rev.* **107**, 664 (1957).

<sup>6</sup> G. Baym, *Phys. Rev.* **121**, 741 (1961).

<sup>7</sup> M. A. Krivoglaz, *Zh. Eksperim. i Teor. Fiz.* **40**, 1812 (1961) [translation: *Soviet Phys.—JETP* **13**, 1273 (1961)].

<sup>8</sup> A. A. Maradudin and A. E. Fein, *Phys. Rev.* **128**, 2589 (1962).

The corrections turn out to be small, but the variation of the Debye-Waller factor from the Gaussian form which is predicted has been noted by experimentalists, although no details are available.

## II. FORMULATION OF THE PROBLEM

The coherent scattering cross section for slow-neutrons incident on a single crystal may be expressed as the Fourier transform of a correlation function as follows:

$$\langle l \rangle^2 \sum_{n,m} \exp[-i\mathbf{K} \cdot (\mathbf{a}_n - \mathbf{a}_m)] \int dt \exp[i\omega(t-t')] \times \langle \exp[-i\mathbf{K} \cdot \mathbf{u}_n(t)] \exp[i\mathbf{K} \cdot \mathbf{u}_m(t')] \rangle_\beta. \quad (1)$$

The interaction is represented by the Fermi pseudo-potential and only single scattering is considered. Certain kinematical factors have been omitted as they do not enter the discussion. The crystal is taken to have one atom per unit cell, for simplicity,  $\langle l \rangle$  is an average of the scattering length over all the atoms,  $\mathbf{a}_n$  and  $\mathbf{u}_n$  are the lattice vector to the site  $\mathbf{n}$  and the displacement from equilibrium of the atom at that site, respectively.  $\mathbf{K}$  and  $\omega$  represent the momentum and energy transfer of the neutron due to the scattering.

Suppose that the Hamiltonian of the crystal is  $H$ . Baym's variational derivative technique then follows upon consideration of the development of the system under the fictitious Hamiltonian

$$H + \sum_n e^{iHt} \mathbf{J}_n \cdot \mathbf{u}_n e^{-iHt}.$$

After time  $t = \text{Re}\tau$ , an eigenstate of  $H$  at  $t=0$ , i.e.,  $|0\rangle$  will have developed into the state

$$|\text{Re}\tau\rangle = \exp(-iH \text{Re}\tau) T_J(\text{Re}\tau, 0) |0\rangle,$$

where

$$T_J(t, t') = P \exp \left\{ -i \sum_n \int_{t'}^t \mathbf{J}_n(t'') \cdot \mathbf{u}_n(t'') dt'' \right\},$$

$P$  denoting the time-ordered exponential.

Defining the matrix element

$$\langle \tau | X(t) | 0 \rangle_J = \text{Tr} e^{-iH\tau} T_J(\text{Re}\tau, t) X(t) T_J(t, 0) \quad (\text{Re}\tau > t > 0),$$

it is shown that the correlation function in (1) may be obtained from the ratio  $\langle \tau | 0 \rangle_J / \langle \tau | 0 \rangle_0$  on setting  $\mathbf{J}_i(t) = \mathbf{K} \{ \delta_{in} \delta(t-t') - \delta_{in} \delta(t') \}$  and analytically continuing the variable  $\tau$  to  $i\beta$ .

In view of the fact that in the harmonic case the correlation function in question contains an exponential factor, the Debye-Waller factor, one writes down a functional expansion of  $\ln \langle \tau | 0 \rangle_J$  in terms of  $\mathbf{J}$ . The required variational derivatives may easily be calculated from the integral equation which the  $T$  operator

satisfies, i.e.,

$$T_{J+\delta J} = T_J - i \int_0^t T_J(t, t') \sum_n \delta \mathbf{J}_n(t') \cdot \mathbf{u}_n(t') T_{J+\delta J}(t', 0) dt'.$$

The first- and second-variational derivatives of  $\ln \langle \tau | 0 \rangle_J$  are

$$i \frac{\delta}{\delta \mathbf{J}_l(t)} \ln \langle \tau | 0 \rangle_J = \frac{\langle \tau | \mathbf{u}_l(t) | 0 \rangle_J}{\langle \tau | 0 \rangle_J} \equiv \mathbf{x}_l(t), \quad (2)$$

and

$$i \frac{\delta}{\delta \mathbf{J}_l(t)} i \frac{\delta}{\delta \mathbf{J}_m(s)} \ln \langle \tau | 0 \rangle_J = \frac{\langle \tau | P(\mathbf{u}_l(t) T(t, s) \mathbf{u}_m(s)) | 0 \rangle_J}{\langle \tau | 0 \rangle_J} - \mathbf{x}_l(t) \mathbf{x}_m(s). \quad (3)$$

If the assumption is now made that the first variational derivative is a linear functional of  $J$ , one obtains Baym's result, namely, that

$$\ln \langle \exp[i\mathbf{K} \cdot \mathbf{u}_n(t)] \exp[-i\mathbf{K} \cdot \mathbf{u}_m(0)] \rangle_\beta = -\langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle_\beta + \langle \mathbf{K} \cdot \mathbf{u}_n(t) \mathbf{K} \cdot \mathbf{u}_m(0) \rangle_\beta.$$

On intuitive grounds we are led to regard  $\mathbf{x}_l(t)$  as the displacement of atom  $\mathbf{l}$  under the influence of the external force  $\mathbf{J}$ . If the atoms are bound in the lattice by harmonic forces, then it is natural to suppose the relationship should be linear; but, in general, this conclusion is not correct. It is possible to show the functional dependence of  $\mathbf{x}_l(t)$  on  $\mathbf{J}$  by writing down the differential equation which it satisfies using the Heisenberg equations of motion. One obtains

$$M_l \ddot{\mathbf{x}}_l(t) = i \langle \tau | [H + \sum_n \mathbf{J}_n(t) \cdot \mathbf{u}_n(t), \mathbf{p}_l(t)] | 0 \rangle_J \langle \tau | 0 \rangle_J^{-1},$$

where  $\mathbf{p}_l$  is the momentum operator conjugate to  $\mathbf{u}_l$ ,  $M_l$  is the mass of atom at site  $\mathbf{l}$ . Taking the potential energy of the lattice to be

$$V = \frac{1}{2} \sum_{j,k} \mathbf{A}_{jk} \mathbf{u}_j \mathbf{u}_k + \frac{1}{6} \lambda \sum_{j,k,l} \mathbf{B}_{jkl} \mathbf{u}_j \mathbf{u}_k \mathbf{u}_l, \quad (4)$$

we see that for harmonic forces the equation for  $\mathbf{x}_l(t)$  is simply

$$M_l \ddot{\mathbf{x}}_l(t) = -\mathbf{J}_l(t) - \sum_k \mathbf{A}_{kl} \mathbf{x}_k(t),$$

which is linear. We can, therefore, assert that Baym's result is correct for a perfect crystal (harmonic) and for one with impurities or vacant lattice sites provided that the interatomic forces are still of "Hookes-law" type. Metals are excluded since the coupling of the conduction electrons to the lattice vibrations destroys the linearity of the equations.

## III. INCLUSION OF THE CUBIC-ANHARMONIC TERM TO SECOND ORDER IN THE COUPLING

Baym's result is, in fact, the leading term in the expansion of  $\ln \langle \exp[i\mathbf{K} \cdot \mathbf{u}_n(t)] \exp[-i\mathbf{K} \cdot \mathbf{u}_m(0)] \rangle$  in powers of  $\mathbf{K}$ . Further terms of the series may be obtained by a straightforward differentiation or alternatively by cal-

culating the higher terms in the functional expansion of  $\ln\langle\tau|0\rangle_J$ . This last procedure can however be made to give some useful identities concerning correlation functions for the harmonic crystal.

The analytic behavior of certain expressions may be found by going to the limit of zero coupling, e.g., there occurs the Fourier transform of the correlation function  $\langle\mathbf{K}\cdot\mathbf{u}_n(t)[\mathbf{K}\cdot\mathbf{u}_m(0)]^3\rangle$  which, for a harmonic crystal factorizes into  $3\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle\langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle$  whose transform is a multiple of the single-phonon peak. We, therefore, conclude that the first function has a resonance character in the fully interacting crystal.

Including the cubic anharmonic term in the Hamiltonian leads to the following equation of motion for  $\mathbf{x}_i(t)$ :

$$M_i\ddot{\mathbf{x}}_i(t) = -\mathbf{J}_i(t) - \sum_k \mathbf{A}_{ki}\mathbf{x}_k - \frac{\lambda}{2} \sum_{i,k} \mathbf{B}_{ijk} \frac{\langle\tau|\mathbf{u}_j(t)\mathbf{u}_k(t)|0\rangle_J}{\langle\tau|0\rangle_J}.$$

From the form of the second-variational derivative of  $\langle\tau|0\rangle$ , we have

$$\langle\tau|\mathbf{u}_j(t)\mathbf{u}_k(t)|0\rangle_J \langle\tau|0\rangle_J^{-1} = \mathbf{x}_k(t)\mathbf{x}_j(t) + i \frac{\delta}{\delta\mathbf{J}_j(t)} \mathbf{x}_k(t).$$

By means of Fourier transformation and diagonalization of the equations of motion which of course leaves the functional dependence on  $J$  unaltered, they may be written symbolically as

$$\mathbf{x} = \mathbf{J} + \lambda \left( \mathbf{x} * \mathbf{x} + \frac{\delta}{\delta\mathbf{J}} \mathbf{x} \right). \quad (5)$$

Here the asterisk denotes a convolution integral.

Iteration of (5) in powers of  $\lambda$  shows that in the absence of the  $\delta\mathbf{x}/\delta\mathbf{J}$  term,  $\mathbf{x}$  is a functional of  $\mathbf{J}$  of degree  $n$  correct to  $O(\lambda^{n-1})$ . The presence of the  $\delta\mathbf{x}/\delta\mathbf{J}$  term does not raise the functional degree of a given order in  $\lambda$ , but the term  $O(\lambda^{n-1})$  will contain, in addition to the part of degree  $n$ , parts of lower degree. This means that the expansion of  $\ln\langle\tau|0\rangle_J$  carried to the fourth-variational derivative will be correct to order  $\lambda^2$ . Note that all this refers to the cubic anharmonic term. It is easily verified that the quartic term in the potential would only be treated in first order by an expansion terminating at  $\mathbf{J}^4$ .

After some algebra one can obtain the equation

$$\begin{aligned} \ln\langle\exp[-i\mathbf{K}\cdot\mathbf{u}_n(t)] \exp[i\mathbf{K}\cdot\mathbf{u}_m(0)]\rangle \\ = -\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle + \langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle + \frac{1}{2}i\langle\mathbf{K}\cdot\mathbf{u}_n(t)(\mathbf{K}\cdot\mathbf{u}_m(0))^2\rangle - \frac{1}{2}i\langle(\mathbf{K}\cdot\mathbf{u}_n(t))^2\mathbf{K}\cdot\mathbf{u}_m(0)\rangle \\ + 1/24\{2\langle(\mathbf{K}\cdot\mathbf{u})^4\rangle - 4\langle\mathbf{K}\cdot\mathbf{u}_n(t)(\mathbf{K}\cdot\mathbf{u}_m(0))^3\rangle + 6\langle(\mathbf{K}\cdot\mathbf{u}_n(t))^2(\mathbf{K}\cdot\mathbf{u}_m(0))^2\rangle - 4\langle(\mathbf{K}\cdot\mathbf{u}_n(t))^3\mathbf{K}\cdot\mathbf{u}_m(0)\rangle - 12\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle^2 \\ + 24\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle\langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle - 12\langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle^2\}. \quad (6) \end{aligned}$$

Consider first the terms of fourth degree in  $K$  which may be regrouped as follows:

$$\begin{aligned} C_1 &= \frac{1}{12}\langle(\mathbf{K}\cdot\mathbf{u})^4\rangle - \frac{1}{4}\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle^2, \\ C_2 &= \langle(\mathbf{K}\cdot\mathbf{u})^2\rangle\langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle - \frac{1}{6}\langle\mathbf{K}\cdot\mathbf{u}_n(t)(\mathbf{K}\cdot\mathbf{u}_m(0))^3\rangle - \frac{1}{6}\langle(\mathbf{K}\cdot\mathbf{u}_n(t))^3\mathbf{K}\cdot\mathbf{u}_m(0)\rangle, \\ C_3 &= \frac{1}{4}\langle(\mathbf{K}\cdot\mathbf{u}_n(t))^2(\mathbf{K}\cdot\mathbf{u}_m(0))^2\rangle - \frac{1}{4}\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle^2 - \frac{1}{2}\langle\mathbf{K}\cdot\mathbf{u}_n(t)\mathbf{K}\cdot\mathbf{u}_m(0)\rangle^2. \end{aligned}$$

In the harmonic approximation  $C_1$ ,  $C_2$ , and  $C_3$  separately vanish. However, when anharmonicities are included, the time-independent  $C_1$  represents part of the new Debye-Waller factor

$$F = \exp[-\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle + \frac{1}{12}\langle(\mathbf{K}\cdot\mathbf{u})^4\rangle - \frac{1}{4}\langle(\mathbf{K}\cdot\mathbf{u})^2\rangle^2 + \dots].$$

The Fourier transform of  $C_2$  will have a resonance character as mentioned in the second paragraph of this section. It is assumed that  $C_3$ , being of "two-phonon" character, does not contribute to the one-phonon peak.

At the moment it is not clear whether or not the Fourier transform of terms of degree  $K^3$  give a contribution to the one-phonon peak, because each term vanishes in the zero coupling limit. We assume that there is a contribution and this will subsequently be verified.

The singular part of the inelastic cross section may be thus be written

$$F(S_{11} + \text{Re}S_{21} + \langle(\mathbf{K}\cdot\mathbf{u})^2\rangle S_{11} - \frac{1}{3} \text{Re}S_{13}), \quad (7)$$

where

$$\begin{aligned} S_{pq} &= \sum_{m,n} \exp[i\mathbf{K}\cdot(\mathbf{a}_n - \mathbf{a}_m)] (-i)^{p+q} \\ &\times \int e^{i\omega t} dt \langle(\mathbf{K}\cdot\mathbf{u}_n(t))^p (\mathbf{K}\cdot\mathbf{u}_m(0))^q\rangle. \quad (8) \end{aligned}$$

The elastic part is

$$F\delta(\omega) \left| \sum_n \exp(i\mathbf{K}\cdot\mathbf{a}_n) \right|^2.$$

#### IV. TREATMENT OF THE CORRELATION FUNCTIONS

The correlation functions are obtained in this section by finding the spectral representation of the related Green's function. Details of the formalism may be found in the literature (e.g., Zubarev<sup>9</sup>) and so will not be reproduced here. Briefly the procedure will be to calculate the Fourier transform of the retarded Green's

<sup>9</sup> D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [translation: Soviet Phys.—Usp. **3**, 320 (1960)].

function  $G(\omega)$  then evaluate

$$\lim_{\epsilon \rightarrow 0} \frac{G(\omega+i\epsilon) - G(\omega-i\epsilon)}{-i(1-e^{-\beta\omega})} \quad (9)$$

for the spectral density function  $\rho(\omega)$ .

In terms of phonon annihilation and creation operators the atomic displacements may be expressed as

$$\mathbf{u}_n = \sum_{\mathbf{f},s} \mathbf{v}(\mathbf{f},s) (2M\omega_{\mathbf{f}s})^{-1/2} (a_{\mathbf{f},s} + a_{-\mathbf{f},s}^\dagger) e^{-i\mathbf{f}\cdot\mathbf{a}_n}, \quad (\hbar=1).$$

For convenience, we define the operators

$$A_{\mathbf{f}s} = a_{\mathbf{f}s} + a_{-\mathbf{f}s}^\dagger; \quad B_{\mathbf{f}s} = a_{\mathbf{f}s} - a_{-\mathbf{f}s}^\dagger.$$

The Hamiltonian is

$$H = \sum_{\mathbf{f}s} \omega_{\mathbf{f}s} a_{\mathbf{f}s}^\dagger a_{\mathbf{f}s} + \frac{1}{6} \sum b(\mathbf{f}s, \mathbf{f}'s', \mathbf{f}''s'') A_{\mathbf{f}s} A_{\mathbf{f}'s'} A_{\mathbf{f}''s''}$$

where

$$b(\mathbf{f}s, \mathbf{f}'s', \mathbf{f}''s'') = \sum \mathbf{B}_{ijk} \mathbf{v}(\mathbf{f}s) \mathbf{v}(\mathbf{f}'s') \mathbf{v}(\mathbf{f}''s'') \times \exp[i(\mathbf{f}\cdot\mathbf{a}_i + \mathbf{f}'\cdot\mathbf{a}_j + \mathbf{f}''\cdot\mathbf{a}_k)] \times (8M^3 \omega_{\mathbf{f}s} \omega_{\mathbf{f}'s'} \omega_{\mathbf{f}''s''})^{-1/2}.$$

Assuming cyclic boundary conditions, the dominant contribution to the one-phonon peak becomes

$$S_{11}(\mathbf{K}, \omega) = N^2 \sum_{s,s'} \frac{\mathbf{K}\cdot\mathbf{v}(\mathbf{K}s) \mathbf{K}\cdot\mathbf{v}^*(\mathbf{K}s')}{2M(\omega_{\mathbf{K}s} \omega_{\mathbf{K}s'})^{1/2}} \times \int e^{-i\omega t} dt \langle A_{\mathbf{K}s}(t) A_{-\mathbf{K}s'}(0) \rangle_\beta.$$

We first observe that the terms in this sum with  $s \neq s'$  will be of second order since two "three-phonon processes" are required in order to change the polarization index of a phonon. Defining the retarded Green's function

$$G_{ss'}(t) = -i\theta(t) \langle [A_{\mathbf{K}s}(t), A_{-\mathbf{K}s'}(0)] \rangle_\beta,$$

we write down the differential equation which it satisfies, i.e.,

$$-\left(\frac{d^2}{dt^2} + \omega_{\mathbf{K}s}^2\right) G_{ss'} = 2\omega_{\mathbf{K}s} \delta(t) \delta_{ss'} - i\omega_{\mathbf{K}s} \theta(t) \sum_{f_1 f_2} b(f_1 s_1; f_2 s_2; -\mathbf{K}s) \times \langle [A_{f_1 s_1}(t) A_{f_2 s_2}(t), A_{-\mathbf{K}s'}(0)] \rangle_\beta.$$

In addition to the new function

$$\mathfrak{K}(f_1 s_1, f_2 s_2, -\mathbf{K}s') = -i\theta(t) \langle [A_{f_1 s_1}(t) A_{f_2 s_2}(t), A_{-\mathbf{K}s}(0)] \rangle_\beta,$$

it is convenient to define

$$\mathfrak{K}(f_1 s_1, f_2 s_2, -\mathbf{K}s) = -i\theta(t) \langle [B_{f_1 s_1}(t) B_{f_2 s_2}(t), A_{-\mathbf{K}s}(0)] \rangle_\beta.$$

Their equations of motion are

$$-\left(\frac{d^2}{dt^2} + \omega_1^2 + \omega_2^2\right) \mathfrak{K}(1, 2, -\mathbf{K}s) = 2\omega_1 \omega_2 \mathfrak{K} + \omega_1 V_{12}(t) + \omega_2 V_{21}(t)$$

$$-\left(\frac{d^2}{dt^2} + \omega_1^2 + \omega_2^2\right) \mathfrak{K}(1, 2, -\mathbf{K}s) = 2\omega_1 \omega_2 \mathfrak{K} + \omega_1 V_{21}(t) + \omega_2 V_{12}(t)$$

$$V_{12}(t) \equiv V(f_1 s_1; f_2 s_2; -\mathbf{K}s) = -i\theta(t) \sum_{q_1 q_2} b(q_1 j_1, q_2 j_2, -f_1 s_1) \langle \langle A_{q_1 j_1} A_{q_2 j_2} A_{f_2 s_2}; A_{-\mathbf{K}s} \rangle \rangle.$$

The notation  $\langle \langle ; \rangle \rangle$  represents the thermal average of the commutator. In terms of the Fourier transforms, the solution to the above is

$$\mathfrak{K}(1, 2, -\mathbf{K}s) = \frac{1}{2} [V_{12}(\omega) + V_{21}(\omega)] \frac{\omega_1 + \omega_2}{\omega^2 - (\omega_1 + \omega_2)^2} + \frac{1}{2} [V_{12}(\omega) - V_{21}(\omega)] \frac{\omega_1 - \omega_2}{\omega^2 - (\omega_1 - \omega_2)^2}.$$

Replacing  $V_{12}(\omega)$  and  $V_{21}(\omega)$  by their decoupled forms we obtain, correct to second order

$$\mathfrak{K}(1, 2, -\mathbf{K}s; \omega) = 2F(f_1 s_1, f_2 s_2, \omega) \sum_j b(-f_1 s_1 - f_2 s_2, \mathbf{K}j) G_{js'}(\omega),$$

where

$$F(1, 2, \omega) = \langle n_1 + n_2 + 1 \rangle \frac{\omega_1 + \omega_2}{\omega^2 - (\omega_1 + \omega_2)^2} + \langle n_1 - n_2 \rangle \frac{\omega_1 - \omega_2}{\omega^2 - (\omega_1 - \omega_2)^2}. \quad (10)$$

Writing now

$$R(\mathbf{K}s, \omega) = \omega^2 - \omega_{\mathbf{K}s}^2 - 2\omega_{\mathbf{K}s} \sum_{f_1 f_2} F(1, 2, \omega) |b(1, 2, \mathbf{K}s)|^2 = \omega^2 - \omega_{\mathbf{K}s}^2 - 2\omega_{\mathbf{K}s} C_{\mathbf{K}s}(\omega),$$

the equation for  $G(\omega)$  may be written as

$$R(Ks, \omega)G_{ss'} = 2\omega_{Ks}\delta_{ss'} + 2\omega_{Ks} \sum_{f_1 f_2} F(1, 2, \omega) \sum_{j \neq s} b(1, 2, Ks)b^*(1, 2, Kj)G_{js'}(\omega). \quad (11)$$

Upon setting  $s' = s$ , the Green's function on the right-hand side of (11) involves polarization changes so that those terms contribute a fourth-order effect.

$$G_{ss}(\omega) = 2\omega_{Ks}\{R(Ks, \omega)\}^{-1}. \quad (12)$$

If  $s' \neq s$ , the dominant term of (11) is the one with  $j = s'$ , therefore,

$$G_{ss'}(\omega) = G_{ss}(\omega)G_{s's'}(\omega) \sum_{f_1 f_2} F(f_1 f_2 \omega) b(f_1 f_2 - Ks)b(-f_1 - f_2 Ks'). \quad (13)$$

Strictly, this method of approximation is valid only provided that  $R(K, \omega)$  is  $o(1)$ . Near  $\omega = \omega_{Ks}$  this is not the case, but it may be shown that then the solutions are still well approximated by the above formulas.

Before calculating  $\rho(\omega)$  from the prescription stated above (9), we first notice that (12) may be expressed (to second order) as

$$G_{ss}(\omega) = [1 + \omega_{Ks}^{-1}C_{Ks}(\omega)]^\dagger [\omega - \omega_{Ks} - C_{Ks}(\omega)]^{-1} - [\omega + \omega_{Ks} + C_{Ks}(\omega)]^{-1}.$$

If  $C_{Ks}(\omega + i\epsilon) = \Delta_{Ks}(\omega) - i\Gamma_{Ks}(\omega)$  in which

$$\Delta_{Ks}(\omega) = P \sum_{f_1 f_2} F(f_1 s_1, f_2 s_2, \omega) |b(f_1 s_1 f_2 s_2 Ks)|^2,$$

$$\Gamma_{Ks}(\omega) = \frac{1}{2}\pi \sum_{f_1 f_2} |b(f_1 s_1 f_2 s_2 Ks)|^2 \{ \langle n_1 + n_2 + 1 \rangle [\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] + \langle n_1 - n_2 \rangle [\delta(\omega - \omega_1 + \omega_2) - \delta(\omega + \omega_1 - \omega_2)] \}. \quad (14)$$

We obtain for  $\rho_{Ks}(\omega)$

$$(1 - e^{-\beta\omega})^{-1} \frac{2\Gamma_{Ks}[1 - (\omega - \omega_{Ks})/\omega_{Ks}]}{(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2} + (e^{-\beta\omega} - 1)^{-1} \frac{2\Gamma_{Ks}[1 + (\omega + \omega_{Ks})/\omega_{Ks}]}{(\omega + \omega_{Ks} + \Delta_{Ks})^2 + \Gamma_{Ks}^2}. \quad (15)$$

In the limit of zero coupling this reduces to the familiar result

$$2\pi\delta(\omega - \omega_{Ks})\langle n_{Ks} + 1 \rangle + 2\pi\delta(\omega + \omega_{Ks})\langle n_{Ks} \rangle.$$

Assuming that  $\Delta(\omega)$  and  $\Gamma(\omega)$  are slowly varying functions of  $\omega$ , then  $\rho(\omega)$  is seen to be a sum of two modified Lorentzian curves, each of width  $\Gamma_{Ks}$  centered about the points  $\pm(\omega_{Ks} + \Delta_{Ks})$ .

The expressions resemble closely the second-order perturbation energy correction and a transition probability, respectively. If we were to write expressions for the energy correction  $\delta_{Ks}$  for the mode  $(\mathbf{K}, s)$  and the total transition probability  $\gamma_{Ks}$  for this mode due to the "three-phonon processes" then we should find that in place of the expectation values of the number operators in (14) there would appear

$$n_K(n_1 + 1)(n_2 + 1) - (n_K + 1)n_1 n_2$$

and

$$n_K n_1 (n_2 + 1) - (n_K + 1)(n_1 + 1)n_2$$

so that

$$\Delta_{Ks} = \delta(n_{Ks} + 1) - \delta(n_{Ks}); \quad \Gamma_{Ks} = \gamma(n_{Ks} + 1) - \gamma(n_{Ks}),$$

which is a particular case of Brout's result.

### A. First-Order Correction to the One-Phonon Peak

This is given by

$$-F \operatorname{Im} \sum_{q_1 q_2 q_3} \prod_i \frac{\mathbf{K} \cdot \mathbf{v}(q_i s_i)}{(2M\omega_{q_i s_i})^{1/2}} D(K - q_1 - q_2) D^*(K + q_3) \times \int e^{i\omega t} dt \langle A_{q_1}(t) A_{q_2}(t) A_{q_3}(0) \rangle_\beta. \quad (16)$$

The diffraction-pattern functions lead to wave-conservation requirement:

$$\mathbf{K} = \mathbf{q}_1 + \mathbf{q}_2; \quad \mathbf{K} = -\mathbf{q}_3.$$

It is now apparent that we have to deal with  $\mathcal{E}(q_1 s_1 q_2 s_2 - K s_3)$ . Correct to second order  $\mathcal{E}(\omega)$  has been calculated in the previous section to be

$$2F(q_1 s_1 q_2 s_2 \omega) b(-q_1 s_1 - q_2 s_2 K s_3) G_{s_3 s_3}(\omega).$$

The presence of the last factor  $G(\omega)$  relating to a phonon  $(\mathbf{K}, s_3)$  justifies the assertion that  $S_{12}(\mathbf{K}\omega)$  contributes to the "one-phonon" peak. In (16) evaluation of the summations over  $q_1, q_2$  for  $\omega$  just above the real axis will give

$$\theta_{K s_3}(\omega) - i\varphi_{K s_3}(\omega),$$

where

$$\theta_{Ks_3}(\omega) = P \sum_{q_1 q_2} \frac{\mathbf{K} \cdot \mathbf{v}(q_1 s_1) \mathbf{K} \cdot \mathbf{v}(q_2 s_2)}{2M(\omega_{q_1 s_1} \omega_{q_2 s_2})^{1/2}} 2F(q_1 s_1 q_2 s_2 \omega) b(-q_1 s_1 - q_2 s_2 K s_3),$$

$$\varphi_{Ks_3}(\omega) = \pi \sum_{q_1 q_2} \frac{\mathbf{K} \cdot \mathbf{v}(q_1 s_1) \mathbf{K} \cdot \mathbf{v}(q_2 s_2)}{2M(\omega_{q_1 s_1} \omega_{q_2 s_2})^{1/2}} b(-q_1 s_1 - q_2 s_2 K s_3)$$

$$\times \{ \langle n_1 + n_2 + 1 \rangle [\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] + \langle n_1 - n_2 \rangle [\delta(\omega - \omega_1 + \omega_2) - \delta(\omega + \omega_1 - \omega_2)] \}.$$

Expression (16) becomes

$$-F \text{Im} N^2 \sum_{s_3} \frac{\mathbf{K} \cdot \mathbf{v}^*(K s_3)}{(2M\omega_{Ks_3})^{1/2}} \rho_{Ks_3}^{(3)}(\omega),$$

where

$$\rho_{Ks}^{(3)}(\omega) = \frac{2\theta_{Ks} \Gamma_{Ks} [1 - (\omega - \omega_{Ks})/\omega_{Ks}] + \varphi_{Ks}(\omega - \omega_{Ks} - \Delta_{Ks})}{[(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2] (1 - e^{-\beta\omega})} + \frac{2\theta_{Ks} \Gamma_{Ks} [1 + (\omega + \omega_{Ks})/\omega_{Ks}] - \varphi_{Ks}(\omega + \omega_{Ks} + \Delta_{Ks})}{[(\omega + \omega_{Ks} + \Delta_{Ks})^2 + \Gamma_{Ks}^2] (e^{-\beta\omega} - 1)}.$$

Higher order terms involving  $\Delta^2$  and  $\Gamma^2$  have been neglected in the numerators. Because of the algebraic property of Lorentzian-type expressions,  $\rho_{Ks}^{(3)}(\omega)$  is given to a good approximation by

$$\rho_{Ks}^{(3)}(\omega) = \theta_{Ks} \rho_{Ks}(\omega) + \varphi_{Ks} \left[ \frac{(\omega - \omega_{Ks} - \Delta_{Ks})(1 - e^{-\beta\omega})^{-1}}{(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2} - \frac{(\omega + \omega_{Ks} + \Delta_{Ks})(e^{-\beta\omega} - 1)^{-1}}{(\omega + \omega_{Ks} + \Delta_{Ks})^2 + \Gamma_{Ks}^2} \right]$$

$$= \theta_{Ks} \rho_{Ks}(\omega) + \varphi_{Ks} \sigma_{Ks}(\omega). \tag{17}$$

The one-phonon peak is accordingly represented by

$$FN^2 \sum_s \frac{|\mathbf{K} \cdot \mathbf{v}(Ks)|^2}{2M\omega_{Ks}} \left[ 1 - \text{Im} \frac{(2M\omega_{Ks})^{1/2}}{\mathbf{K} \cdot \mathbf{v}(Ks)} \theta_{Ks} \right] \rho_{Ks}(\omega),$$

which may be interpreted by saying that the Debye-Waller factor for the "one-phonon" part of the spectrum differs from that for the elastic part by the factor

$$1 - \text{Im}(2M\omega_{Ks})^{1/2} [\mathbf{K} \cdot \mathbf{v}(Ks)]^{-1} \theta_{Ks}, \tag{18}$$

now depending explicitly on polarization through a correction term which is first order in the coupling constant.

We have so far neglected the terms in  $\varphi_{Ks}(\omega)$  which involve the function of  $\sigma_{Ks}(\omega)$ . This part has an asymmetric character which tends to distort the Lorentzian shape of the main curve. The width of the curve is only affected in higher order, but there will be a contribution to the height of order  $\varphi_{Ks}$ . Thus, when the anharmonicities are appreciable it is clear that the profile will no longer be a simple Lorentz shape.

**B. Second-Order Corrections**

In view of the remark at the end of the last section, it might seem that a discussion of second-order corrections to the "one-phonon" profile is rather academic; however, for a Bravais-type lattice these first-order corrections vanish identically so that it is the second-order corrections which may be important. These will come from the off-diagonal Green's functions  $G_{ss'}(\omega)$  in (13) and also from the fourth derivative of  $\ln \langle \tau | 0 \rangle_J$  which we

consider first, i.e.,

$$F \cdot [ \langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle S_{11} - \frac{1}{3} S_{13} ]. \tag{19}$$

We discuss the equation satisfied by the Green's function  $G^{(4)}(t)$

$$G^{(4)}(t) = -i\theta(t) \langle \langle A_1; A_2 A_3 A_4 \rangle \rangle,$$

$$-(d^2/dt^2 + \omega_1^2) G^{(4)} = \omega_1 \delta(t) \langle \langle B_1; A_2 A_3 A_4 \rangle \rangle \tag{20}$$

$$+ \omega_1 \sum_{q_1 q_2} b(q_1 q_2 - f_1) H(q_1 q_2 f_2 f_3 f_4).$$

As before, it is convenient to define the functions

$$H(q_1 q_2 f_2 f_3 f_4) = -i\theta(t) \langle \langle A_{q_1} A_{q_2}; A_{f_2} A_{f_3} A_{f_4} \rangle \rangle$$

$$K(q_1 q_2 f_2 f_3 f_4) = -i\theta(t) \langle \langle B_{q_1} B_{q_2}; A_{f_2} A_{f_3} A_{f_4} \rangle \rangle.$$

$H$  and  $K$  satisfy differential equations similar in form to (9), but we now find extra terms from the nonvanishing of certain expectation values.

$$-(d^2/dt^2 + \omega_1^2 + \omega_2^2) H$$

$$= 2\omega_1 \omega_2 K + \omega_1 U_{12} + \omega_2 U_{21} + \delta(t) \{ \omega_1 \langle A_2 [B_1, A_{f_2} A_{f_3} A_{f_4}] \rangle$$

$$+ \omega_2 \langle A_1 [B_2, A_{f_2} A_{f_3} A_{f_4}] \rangle \}, \tag{21}$$

$$-(d^2/dt^2 + \omega_1^2 + \omega_2^2) K$$

$$= 2\omega_1 \omega_2 H + \omega_1 U_{21} + \omega_2 U_{12} + \delta(t) \{ \omega_1 \langle A_1 [B_2, A_{f_2} A_{f_3} A_{f_4}] \rangle$$

$$+ \omega_2 \langle A_2 [B_1, A_{f_2} A_{f_3} A_{f_4}] \rangle \}$$

$$+ i \frac{d}{dt} \delta(t) \langle [B_1 B_2, A_{f_2} A_{f_3} A_{f_4}] \rangle, \tag{22}$$

where

$$U_{12}(t) = -i\theta(t) \sum_{f'f} b(fs f's' - q_1 j_1) \times \langle \langle A_{q_2 j_2} A_{f_3} A_{f's'}; A_{f_2 s_2} A_{f_3 s_3} A_{f_4 s_4} \rangle \rangle.$$

Using the definitions

$$y = \langle [B_{q_1} A_{q_2} + A_{q_1} B_{q_2}, A_{f_2} A_{f_3} A_{f_4}] \rangle, \\ z = \langle [B_{q_1} B_{q_2}, A_{f_2} A_{f_3} A_{f_4}] \rangle,$$

we obtain just as in Sec. IV A by decoupling  $U_{12}(\omega)$

$$H(\omega) = 2F(q_1 q_2 \omega) \sum_j b(-q_1 - q_2 f j) G_j^{(4)}(\omega) \\ + \frac{1}{2} \frac{(\omega_{q_1} + \omega_{q_2})y + \omega z}{\omega^2 - (\omega_{q_1} + \omega_{q_2})^2} - \frac{1}{2} \frac{\omega z}{\omega^2 - (\omega_{q_1} - \omega_{q_2})^2}. \quad (23)$$

The index  $j$  refers to the polarization of  $\mathbf{f}$  in

$$G_j^{(4)} = G^{(4)}(\mathbf{f}j; \mathbf{f}_2 s_2 \mathbf{f}_3 s_3 \mathbf{f}_4 s_4).$$

Correct to second order, Eq. (20) becomes

$$R(f_1 s_1, \omega) G_{s_1}^{(4)}(\omega) \\ = \omega_{f_1 s_1} \langle [B_{f_1 s_1}, A_{f_2} A_{f_3} A_{f_4}] \rangle + \frac{1}{2} \omega_{f_1 s_1} \sum_{q_1 q_2} b(q_1 q_2 - f_1) \\ \times \left[ \frac{(\omega_{q_1} + \omega_{q_2})y + \omega z}{\omega^2 - (\omega_{q_1} + \omega_{q_2})^2} - \frac{\omega z}{\omega^2 - (\omega_{q_1} - \omega_{q_2})^2} \right]. \quad (24)$$

The first term in (19) is cancelled by the first one on the right side of (24). Thus, we obtain for (19)

$$\frac{1}{3} \text{Re} FN^2 \sum_{s_1 f_2 f_3 f_4} \frac{\mathbf{K} \cdot \mathbf{v}(K s_1)}{(2M\omega_{K s_1})^{1/2}} \\ \times \rho_{K s_1}^{(4)}(\omega) \prod_{i=2}^4 \frac{\mathbf{K} \mathbf{v} \cdot (f_i s_i)}{(2M\omega_{f_i s_i})^{1/2}}. \quad (25)$$

$\rho_{K s}^{(4)}(\omega)$  is the density function corresponding to

$$\frac{1}{2} \omega_{K s} \sum_{q_1 q_2} b(q_1 q_2 - K s) \left[ \frac{(\omega_{q_1} + \omega_{q_2})y + \omega z}{\omega^2 - (\omega_{q_1} + \omega_{q_2})^2} - \frac{\omega z}{\omega^2 - (\omega_{q_1} - \omega_{q_2})^2} \right] R(K s, \omega)^{-1}. \quad (26)$$

By the usual argument we find

$$\rho_{K s}^{(4)}(\omega) = \mu(K s f_2 f_3 f_4, \omega) \rho_{K s}(\omega) + \mu'(K s f_2 f_3 f_4, \omega) \sigma_{K s}(\omega),$$

in which  $\mu_{K s}(\omega)$  is the principal part of the numerator in (26) and  $\mu_{K s}'(\omega)$  is its imaginary part.

The other second-order effects come from the off-diagonal Green's functions in  $S_{11}(K\omega)$ , i.e., from the density function corresponding to

$$\sum_{s \neq s'} \frac{\mathbf{K} \cdot \mathbf{v}(K s) \mathbf{K} \cdot \mathbf{v}^*(K s')}{2M(\omega_{K s} \omega_{K s'})^{1/2}} G_{s s'}(\omega). \quad (27)$$

Rewriting (13) as

$$G_{s s'}(\omega) = \frac{4\omega_{K s} \omega_{K s'} \sum_{f_1 f_2} F(f_1 f_2 \omega) b(f_1 f_2 K s) b^*(f_1 f_2 K s')}{(\omega^2 - \omega_{K s}^2 - 2\omega_{K s} C_{K s})(\omega^2 - \omega_{K s'}^2 - 2\omega_{K s'} C_{K s'})},$$

we make use of the algebraic identity

$$4ab(x^2 - a^2)^{-1}(x^2 - b^2)^{-1} \\ \equiv \frac{2b}{a^2 - b^2} \left( \frac{1}{x - a} - \frac{1}{x + a} \right) - \frac{2a}{a^2 - b^2} \left( \frac{1}{x - b} - \frac{1}{x + b} \right)$$

to obtain the approximate relation

$$G_{s s}(\omega) G_{s' s'}(\omega) \\ = 2(\omega_{K s}^2 - \omega_{K s'}^2)^{-1} (\omega_{K s'} G_{s s} - \omega_{K s} G_{s' s'}). \quad (28)$$

We are justified in neglecting certain second-order corrections to the factors multiplying  $G_{s s}$  and  $G_{s' s'}$  in (28) since the whole expression is to be further multiplied by

$$\alpha_{s s'}(\omega) = \sum_{f_1 f_2} F(f_1 f_2 \omega) b(f_1 f_2 K s) b^*(f_1 f_2 K s').$$

In exact analogy with the derivation of (17) and the discussion of (26), the density function corresponding to  $\alpha_{s s'} G_{s s'}$  is given by

$$\nu_{s s'} \rho_{K s}(\omega) + \nu_{s s'}' \sigma_{K s}(\omega),$$

where  $\nu_{s s'}$  and  $\nu_{s s'}'$  are the real and imaginary parts of  $\alpha_{s s'}(\omega + i\epsilon)$ . On inserting this last expression into (27) one obtains as the second-order contribution to  $S_{11}(\mathbf{K}\omega)$

$$4N^2 \text{Re} \sum_{s, s' \neq s} \frac{\mathbf{K} \cdot \mathbf{v}(K s) \mathbf{K} \cdot \mathbf{v}^*(K s')}{2M(\omega_{K s} \omega_{K s'})^{1/2}} \frac{\omega_{K s'}}{\omega_{K s}^2 - \omega_{K s'}^2} \\ \times [\nu_{s s'} \rho_{K s}(\omega) + \nu_{s s'}' \sigma_{K s}(\omega)].$$

## SUMMARY AND CONCLUSION

We have seen that while Baym's treatment is inexact for a crystal with anharmonicities, it does represent a good approximation and is correct for a nonmetallic crystal with harmonic forces. A method of dealing with the case of a crystal with impurities has been indicated by Krivoglaz, although he appears to neglect certain first-order effects associated with the phonon correlation functions  $\langle a_f(t) a_{-f}(0) \rangle$  and  $\langle a_f^\dagger(t) a_{-f}^\dagger(0) \rangle$ . By considering primarily the operators  $A_f$ , these terms are easily included as in the present work.

Generally, the elastic scattering peak is multiplied by a new Debye-Waller factor

$$\exp[-\langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle + \frac{1}{2} \langle (\mathbf{K} \cdot \mathbf{u})^4 \rangle - \frac{1}{4} \langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle^2 + \dots],$$

where the corrections in the exponent are of second order for the particular anharmonic interaction we have considered. It is possible to continue the exponent, in which the next term is

$$(1/360)[\langle (\mathbf{K} \cdot \mathbf{u})^6 \rangle - 15\langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle \langle (\mathbf{K} \cdot \mathbf{u})^4 \rangle + 30\langle (\mathbf{K} \cdot \mathbf{u})^2 \rangle^3]$$

but this represents a fourth-order effect in the present case.

In order to discuss the features of the inelastic scattering one requires, in addition to the one-phonon Green's functions, higher degree correlation functions if the anharmonicity is to be consistently included to any given order. Because of the wave-vector conservation property of the lattice potential it is found that these corrections are associated with a particular phonon wave vector and contain "resonance-denominators." We are thus justified in regarding them as corrections to the "one-phonon" peak.

Although the higher correlation functions contain the resonance factor  $\rho(\omega)$ , they also contribute an asymmetric correction term  $\sigma(\omega)$ . The Lorentzian profile of the cross section is, therefore, distorted and it is no longer strictly correct to regard its width as a direct measure of the phonon lifetime.

The first-order correction to the one-phonon peak, which depends on the integrals  $\theta$  and  $\varphi$ , will vanish identically for a Bravais lattice with a center of symmetry since the polarization vectors  $\mathbf{v}(f,s)$  and the coefficients  $b(\mathbf{f}\mathbf{s}\mathbf{f}'\mathbf{s}'\mathbf{f}''\mathbf{s}'')$  are real in that case. In the case of a more general type of lattice this term need not vanish. In order to estimate the size of this correction for the general case and also the size of the second-order correction which persists even in a Bravais lattice, we recall Eq. (7). This expresses the zero-, first-, and second-order terms of the cross section, respectively, as

$$S_{11}, \text{Re}S_{12}, \langle (\mathbf{K}\cdot\mathbf{u})^2 \rangle S_{11} - \frac{1}{3} \text{Re}S_{13},$$

where the quantities  $S_{pq}$  are defined in (8).

In the Appendix it is argued that the orders of magnitude of these expressions are in the ratios of the quantities

$$\langle (\mathbf{K}\cdot\mathbf{u})^2 \rangle : \langle (\mathbf{K}\cdot\mathbf{u})^3 \rangle : \frac{1}{3} \langle (\mathbf{K}\cdot\mathbf{u})^4 \rangle - \langle (\mathbf{K}\cdot\mathbf{u})^2 \rangle^2.$$

Taking a linear anharmonic-oscillator model represented by a particle in the potential

$$V(x) = Ax^2 - Bx^3,$$

we obtain for the above ratios, using Boltzmann statistics

$$1 : (15/4) |K| B\beta^{-1} A^{-2} : (5/2) |K|^2 B^2 \beta^{-2} A^{-4}.$$

The quantity  $k_B B A^{-2}$  is the coefficient of linear expansion, which is of order  $10^{-4}$  to  $10^{-5}$  per  $^\circ\text{C}$ , so that

$$|K| B\beta^{-1} A^{-2} \approx 10^{-4} T |K| a.$$

" $a$ " is the interatomic spacing ( $|K| \approx a^{-1}$ ). For  $T = 300^\circ\text{K}$ , the ratios become

$$1 : 10^{-2} (10^{-3}) : 10^{-4} (10^{-5}),$$

showing that the correction terms contribute  $\sim 1\%$  or less to the one-phonon peak. This figure is certainly a generous upper limit for the first-order term because the

fact that the first correction vanishes in the case of a Bravais lattice means that in other cases it might still vanish or at least be smaller than the quantity  $|S_{12}|$ .

We can conclude that while the corrections discussed in this work exist they appear to be very small for dielectric crystals. In particular, for the Bravais lattice the correction is negligible ( $\sim 0.01\%$ ).

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#### APPENDIX

From Eq. (8) and using  $a_{fs} + a_{-fs}^+ = A_{fs}$ , we can write

$$S_{1p} = (-i)^{1+p} \sum_{m,n} \exp[-i\mathbf{K}\cdot(\mathbf{a}_n - \mathbf{a}_m)] \\ \times \sum_{f,s} \int e^{i\omega t} \frac{\mathbf{K}\cdot\mathbf{v}(fs)}{(2M\omega_{fs})^{1/2}} \exp(i\mathbf{f}\cdot\mathbf{a}_n) \\ \times \langle A_{fs}(t) (\mathbf{K}\cdot\mathbf{u}_m(0))^p \rangle_{\beta} dt. \quad (\text{A1})$$

Now the Fourier transform of the phonon Green's functions is consistent with the following time dependence for the annihilation and creation operators:

$$a_{fs}(t) = a_{fs} \exp[-i\Gamma_{fs}|t| - i(\omega_{fs} + \Delta_{fs})t].$$

Substitution of these expressions in (A1) gives for the peaks, corresponding to phonon emission,

$$(-i)^{p+1} \sum_{n,m} \exp[-i\mathbf{K}\cdot(\mathbf{a}_n - \mathbf{a}_m)] \\ \times \sum_s \frac{\Gamma_{Ks}}{(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2} \\ \times \sum_f \frac{\mathbf{K}\cdot\mathbf{v}(fs) \exp(i\mathbf{f}\cdot\mathbf{a}_n)}{(2M\omega_{fs})^{1/2}} \langle a_{fs} (\mathbf{K}\cdot\mathbf{u}_m)^p \rangle.$$

The order of magnitude of this quantity is unaltered on replacing  $a_{fs}$  by  $A_{fs}$  in the expectation value. Making this replacement and averaging the sum over  $f$  over polarizations we obtain for the  $(K, s')$  phonon peak

$$(-i)^{p+1} \sum_{n,m} \exp[-i\mathbf{K}\cdot(\mathbf{a}_n - \mathbf{a}_m)] \\ \times \frac{\Gamma_{Ks}}{(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2} \langle \mathbf{K}\cdot\mathbf{u}_n (\mathbf{K}\cdot\mathbf{u}_m)^p \rangle \\ \approx N \frac{\Gamma_{Ks}}{(\omega - \omega_{Ks} - \Delta_{Ks})^2 + \Gamma_{Ks}^2} \langle (\mathbf{K}\cdot\mathbf{u})^{p+1} \rangle.$$