

## Neutron scattering by anharmonic crystals and the effect of sublattice displacements

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**Abstract.** A theory has been given for the scattering of neutrons by anharmonic crystals, for which terms of the type  $V^{(3)}(k_{1j_1}; -k_{1j_1}; 0_j)$  which contribute to the sublattice displacements are not neglected. Using the standard perturbation theory in the interaction picture or Green's function method, an expression has been derived for the differential scattering cross-section which brings in the shift and the width of the phonons in one-phonon energy exchange processes. It is shown that the sublattice displacements will modify the phase factor arising from the scattering by any atom in the unit cell, and the Debye-Waller factor also gets altered both by the sublattice displacements as well as by higher order terms arising from anharmonicity. It is shown that the differential scattering cross-section contains a term linearly depending on the third order anharmonicity coefficient  $V^{(3)}(k_{1j_1}; k_{2j_2}; k_{3j_3})$  and neutron scattering by crystals should provide a useful method for evaluating the third order anharmonicity coefficients.

**Keywords.** Anharmonicity; sublattice displacement; scattering cross-section; third order elastic constants.

### 1. Introduction

Anharmonicity of vibrations in crystals provides two important effects which could be observed in Raman or neutron scattering. Firstly, the frequencies of lattice vibrations suffer a small shift as the temperature is raised and secondly, the spectral lines exhibit a finite width which account for the finite phonon life-time at higher temperatures (Ludwig 1967). Apart from these two effects, anharmonicity also causes sublattice displacements of the interpenetrating Bravais lattices of which the crystal is composed. The contribution of the sublattice displacements to the various physical properties of crystals does not seem to have received much attention in literature even though it is well known that these sublattice displacements play a crucial role in the phase transitions of ferroelectric crystals (Blinic *et al* 1974).

The scattering of neutrons by anharmonic crystals has been studied earlier (Maradudin and Fein 1962; Maradudin and Ambegaokar 1964; Kokkedee 1962; Cowley 1963, 1968; Thompson 1963) and detailed reviews of the subject can be had from text books (Ludwig 1967; Barron and Klein 1974). Kokkedee (1962) has studied the anharmonic effects in the coherent scattering of neutrons by crystals and he has arrived essentially at the same expression for the width and shift of the spectral lines as that of Maradudin and Fein (1962). Using the Green's function method, Cowley (1963, 1968) has also obtained the same expression for the width and shift of the spectral lines. The existing theories on the anharmonic effects of neutron scattering by crystals have been confined to crystals which are either simple Bravais lattices or

for which each atom is at a centre of symmetry. It is therefore essential to have a general theory of neutron scattering by anharmonic crystals, which will bring out explicitly the contributions of the sublattice displacements to the differential scattering cross-section of the crystal as well as the quantum effects of the higher order terms arising from the non-commutability of operators in the presence of anharmonicity. Such a theory will be specifically useful to study the neutron scattering by ferroelectric crystals near the region of the phase transition. For ferroelectric crystals, some of the optical modes corresponding to the wave vector  $q=0$  become soft as the transition temperature is approached from above and the eigen vector corresponding to the soft modes gets frozen in the ferroelectric phase. The phase transition is accompanied by a spontaneous polarisation and sublattice displacements associated with these soft modes. It is clear that any theory of neutron scattering by ferroelectric crystals should take into account the sublattice displacements of the atoms in the unit cell and their contribution to the scattering near the region where phase transition takes place.

The present paper aims at giving a theory of the scattering of neutrons by anharmonic crystals for which the effect of the anharmonicity coefficients of the type  $V^{(3)}(\mathbf{k}_{1j1}; -\mathbf{k}_{1j1}; 0_j)$  which contribute to the sublattice displacements are not ignored. These coefficients were neglected in the earlier treatment by Maradudin and Fein (1962) Kokkedee (1962) and Cowley (1963) and hence their theories could not account for the relative inner displacements of the Bravais lattices. An expression has been given for the differential scattering cross-section by the anharmonic crystal by using the perturbation theory in the interaction picture or the Green's function formalism, and this expression describes the usual Bragg scattering, the one-phonon process and the linewidth and shift of phonons. It is shown that the sublattice displacements will modify the phase factor arising from any atom in the unit cell and the scattering cross-section will depend on the relative sublattice displacements of the primitive lattices. The third order contribution of anharmonicity to the Debye-Waller factor has been evaluated and it is shown that the Debye-Waller factor also gets modified by terms involving the sublattice displacements.

## 2. The differential scattering cross-section

The differential scattering cross-section per unit solid angle and unit interval of outgoing energy of the scattered particle is given by (Maradudin *et al* 1971)

$$\frac{d^2\sigma}{d\Omega dt} = \frac{k}{\hbar k_0} S(\mathbf{k}, \omega), \quad (1)$$

where the scattering function

$$S(\mathbf{k}, \omega) = N \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp \{i\mathbf{k} \cdot [\mathbf{r}(k_2) - \mathbf{r}(k_1)]\} \times \\ \sum_l \exp [i\mathbf{k} \cdot \mathbf{r}(l)] \int \exp(i\omega t) dt \left\langle \exp \left[ -i\mathbf{k} \cdot \mathbf{u} \begin{pmatrix} 0 \\ k_1 \\ 0 \end{pmatrix} \right] \right. \\ \left. \exp \left[ i\mathbf{k} \cdot \mathbf{u} \begin{pmatrix} l \\ k_2 \\ t \end{pmatrix} \right] \right\rangle. \quad (2)$$

In the above we are following the usual notation of lattice dynamics (Maradudin *et al* 1971);  $\mathbf{k}$  is the difference in the wave vectors of the incident and scattered neutrons;  $\mathbf{r}(l)$  is the position vector of the  $l$ th unit cell;  $\mathbf{r}(k)$  is the position vector of the  $k$ th atom in the  $l$ th unit cell;  $\mathbf{u} \left( \begin{smallmatrix} l \\ k \end{smallmatrix} \right)$  denotes the displacement of atom  $k$  in cell  $l$  from its equilibrium value. Further  $\langle \dots \rangle$  denotes the thermal average given by

$$\langle F \rangle = \text{Tr} \exp - (\beta H) F / \text{Tr} \exp - (\beta H), \quad (3)$$

and  $\mathbf{u} \left( \begin{smallmatrix} l_2 \\ k_2 \end{smallmatrix} ; t \right)$  is the time-dependent Heisenberg operator defined by

$$\mathbf{u} \left( \begin{smallmatrix} l_2 \\ k_2 \end{smallmatrix} ; t \right) = \exp (itH/\hbar) \mathbf{u} \left( \begin{smallmatrix} l_2 \\ k_2 \end{smallmatrix} \right) \exp - (itH/\hbar), \quad (4)$$

where  $H$  is the Hamiltonian of the system.

Let us now write the Hamiltonian of the system in the form

$$H = H_0 + H_A, \quad (5)$$

where  $H_0$  is the Hamiltonian in the harmonic approximation and  $H_A$  is the anharmonic Hamiltonian. They are given by

$$H_0 = \frac{1}{2} \sum_{\tilde{\mathbf{k}}j} \{ \dot{Q}^*(\tilde{\mathbf{k}}j) \dot{Q}(\tilde{\mathbf{k}}j) + \omega_j^2(\tilde{\mathbf{k}}) Q^*(\tilde{\mathbf{k}}j) Q(\tilde{\mathbf{k}}j) \} \quad (6)$$

$$\text{and } H_A = \sum_{\mathbf{k}_{1j_1} \mathbf{k}_{2j_2} \mathbf{k}_{3j_3}} V^{(3)}(\mathbf{k}_{1j_1}; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3}) A_{\mathbf{k}_{1j_1}} A_{\mathbf{k}_{2j_2}} A_{\mathbf{k}_{3j_3}} + \sum_{\mathbf{k}_{1j_1} \mathbf{k}_{2j_2} \mathbf{k}_{3j_3} \mathbf{k}_{4j_4}} V^{(4)}(\mathbf{k}_{1j_1}; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3}; \mathbf{k}_{4j_4}) A_{\mathbf{k}_{1j_1}} A_{\mathbf{k}_{2j_2}} A_{\mathbf{k}_{3j_3}} A_{\mathbf{k}_{4j_4}}, \quad (7)$$

$$\text{where } A_{\mathbf{k}j} = a_{-\mathbf{k}j}^+ + a_{\mathbf{k}j}; \quad (8)$$

$a_{-\mathbf{k}j}^+$  and  $a_{\mathbf{k}j}$  represent the phonon creation and annihilation operators respectively. The operators  $V^{(3)}$  and  $V^{(4)}$  satisfy certain symmetry requirements (Born and Huang 1954; Maradudin and Fein 1962).  $V^{(3)}$  is nonzero only when the sum  $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$  or a vector of the reciprocal lattice. Similarly,  $V^{(4)}$  is nonzero only when  $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4 = 0$  or a vector of the reciprocal lattice.

Now let us write

$$A = -i\mathbf{k} \cdot \mathbf{u} \left( \begin{smallmatrix} 0 \\ k_1 \end{smallmatrix} ; 0 \right) = A(0), \quad (9)$$

$$B = i\mathbf{k} \cdot \mathbf{u} \left( \begin{smallmatrix} l \\ k_2 \end{smallmatrix} ; t \right) = B(t). \quad (10)$$

The operators  $A$  and  $B$  do not commute and hence we use the well-known result (Ludwig 1967)

$$\begin{aligned} \langle e^A e^B \rangle &= \exp(-W_A - W_B) \exp \{ \langle AB \rangle - \langle A \rangle \langle B \rangle \\ &+ \frac{1}{2} \langle A^2 B \rangle - \frac{1}{2} \langle A^2 \rangle \langle B \rangle - \langle A \rangle \langle AB \rangle \\ &+ \langle A \rangle^2 \langle B \rangle + \frac{1}{2} \langle AB^2 \rangle - \frac{1}{2} \langle A \rangle \langle B^2 \rangle \\ &- \langle AB \rangle \langle B \rangle + \langle A \rangle \langle B \rangle^2 + \text{higher order terms} \}, \end{aligned} \quad (11)$$

where

$$\begin{aligned} -W_A &= \langle A \rangle + \frac{1}{2} \{ \langle A^2 \rangle - \langle A \rangle^2 \} \\ &+ \frac{1}{6} \{ \langle A^3 \rangle - 3 \langle A \rangle \langle A^2 \rangle + 2 \langle A \rangle^3 \}. \end{aligned} \quad (12)$$

A similar relation holds for  $-W_B$ . For simple Bravais lattices or for crystals for which each atom is at a centre of symmetry, the averages  $\langle A \rangle$  or  $\langle B \rangle$  which depend on the sublattice displacements vanish, but since it is our aim specifically to evaluate the contribution of sublattice displacements for a general non-Bravais crystal, we will not ignore them here and shall study their contribution to neutron scattering.

Our problem therefore reduces to the evaluation of the averages  $\langle A \rangle$ ,  $\langle B \rangle$ ,  $\langle A^2 \rangle$ ,  $\langle B^2 \rangle$ ,  $\langle AB \rangle$ ,  $\langle AB^2 \rangle$ ,  $\langle A^2 B \rangle$ ,  $\langle A^3 \rangle$  and  $\langle B^3 \rangle$ . Now,

$$\begin{aligned} \left\langle \mathbf{u}_\alpha \left( \begin{matrix} l \\ k_1 \end{matrix} \right) \right\rangle &= \frac{\hbar^{3/2}}{(2NM_{k_1})^{1/2}} \sum_{\mathbf{k}j} \frac{\mathbf{e}_\alpha(k_1 | \mathbf{k}j)}{[\omega(\mathbf{k}j)]^{1/2}} \times \\ &\exp [2\pi i \mathbf{k} \cdot \mathbf{x}(l)] \cdot \langle A_{\mathbf{k}j}(0) \rangle \end{aligned} \quad (13)$$

The expectation value of the operator  $A_{\mathbf{k}j}(0)$  has earlier been evaluated (Viswanathan and Watanabe 1966) and this is given by

$$\langle A_{\mathbf{k}j}(0) \rangle = \langle A_{\mathbf{k}j}(\tau) \rangle = - \frac{6}{\hbar \omega(\mathbf{k}j)} \sum_{\mathbf{k}_1 j_1} V^{(3)}(\mathbf{k}_{1j_1}; -\mathbf{k}_{1j_1}; 0_j) \times g_{\mathbf{k}_1 j_1} \quad (14)$$

where  $g_{\mathbf{k}j} = 2n(\mathbf{k}j) + 1$ , (15)

and  $n(\mathbf{k}j) = [\exp(\beta \hbar \omega(\mathbf{k}j)) - 1]^{-1}$ . (16)

The diagram that contributes to  $\langle A_{\mathbf{k}j}(\tau) \rangle$  is given in figure 1. Thus substituting in (9) we find that

$$\langle A \rangle = -i\mathbf{k} \cdot \left\langle \mathbf{u} \left( \begin{matrix} 0 \\ k_1 \end{matrix} ; 0 \right) \right\rangle = -i\mathbf{k} \cdot \langle \mathbf{u}(k_1) \rangle, \quad (17)$$

where the sublattice displacement  $\langle \mathbf{u}(k_1) \rangle$  can be obtained by substituting (14) in

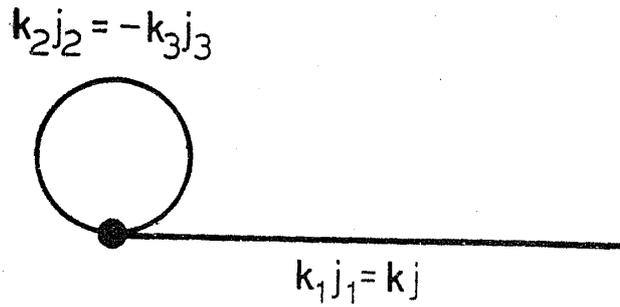


Figure 1. Diagram that contributes to  $\langle A_{kj}(\tau) \rangle$  type averages.

(13). Similarly, the average of the operator  $B$  can also be found to be independent of  $\tau$  and we have

$$\langle B \rangle = ik \cdot \langle \mathbf{u}(k_2) \rangle. \tag{18}$$

These averages depend only on the atom indices  $k_1$  and  $k_2$  and correspond to the sublattice displacements of the Bravais lattices associated with these atoms in the unit cell.

### 3. Thermal averages of the operators $A^2$ , $B^2$ , $AB$ , $A^3$ , $B^3$ , $A^2B$ and $AB^2$

We shall first evaluate the thermal averages of the product of two operators such as  $\langle A^2 \rangle$ ,  $\langle B^2 \rangle$  and  $\langle AB \rangle$ . In the interaction picture, the average of any operator  $O$  is given by

$$\langle O \rangle = \text{Tr} [\exp(-\beta H_0) S(\beta) O] / \text{Tr} [\exp(-\beta H_0) S(\beta)] \tag{19}$$

$$S(\beta) = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int_0^{\beta} \dots \int_0^{\beta} T [H_A(\tau_1) \times H_A(\tau_2) \dots H_A(\tau_n)] d\tau_1, d\tau_2 \dots d\tau_n \tag{20}$$

$$H_A(\tau) = \exp(\tau H_0) H_A \exp(-\tau H_0), \tag{21}$$

and  $T$  is the time ordering operator. Generally the averages of the products of the operators mentioned above can be evaluated by evaluating the thermal average

$$\langle A_{\tilde{\mathbf{k}}\tilde{j}}(\tau_1) A_{\tilde{\mathbf{k}}'\tilde{j}'}(\tau_2) \rangle$$

for different times and later assigning the values 0 or  $\tau$  for  $\tau_1$  and  $\tau_2$ . If we write  $\lambda = \tilde{\mathbf{k}}\tilde{j}$  and  $\lambda' = \tilde{\mathbf{k}}'\tilde{j}'$ , these averages involve the harmonic phonon propagator which is defined by

$$\langle T A_{\lambda}(\tau_1) A_{\lambda'}(\tau_2) \rangle = \delta_{\lambda-\lambda'} \tilde{g}(\lambda, \tau_1 - \tau_2), \tag{22}$$

$$\begin{aligned} \text{where } \tilde{g}(\lambda, \tau) &= \langle TA_\lambda(\tau) A_{-\lambda}(0) \rangle \\ &= n_\lambda \exp(|\tau| \hbar \omega_\lambda) + (n_\lambda + 1) \exp(-|\tau| \hbar \omega_\lambda). \end{aligned} \quad (23)$$

The harmonic phonon propagator is nonzero only when  $\mathbf{k} + \mathbf{k}' = 0$  or  $\mathbf{k}' = -\mathbf{k}$ . Further, the phonon propagator has the following well-known Fourier expansion (Barron and Klein 1974)

$$g(\lambda, \tau) = \sum_{n=-\infty}^{+\infty} g(\lambda, i\omega_n) \exp_{\pm}(i\hbar \omega_n \tau), \quad (24)$$

$$\text{where } g(\lambda, i\omega_n) = \frac{2\omega_\lambda}{\beta \hbar (\omega_\lambda^2 + \omega_n^2)}, \quad (25)$$

$$\text{and } \omega_n = 2\pi n / \beta \hbar. \quad (26)$$

We shall use the linked cluster expansion theorem to evaluate the thermal averages, but to conserve space we shall not give the details of the derivation. It is an important consequence of this theorem that the denominator in (19) will cancel with one of the factors of the numerator and only connected diagrams contribute to the thermal averages. The diagrams that contribute to the third and fourth order anharmonicity terms are shown in figure 2. If we write  $\lambda_1 = \mathbf{k}_{1j_1}$ ,  $\lambda'_1 = \mathbf{k}'_{1j'_1}$ ,  $\lambda_2 = \mathbf{k}_{2j_2}$ , etc. we find that

$$\begin{aligned} \langle B^2(\tau) \rangle &= -\frac{\hbar}{2NM_{k_2}} \sum_{\tilde{\mathbf{k}} j} \frac{\mathbf{k} \cdot \mathbf{e}(k_2 | \tilde{\mathbf{k}} j) \mathbf{k} \cdot \mathbf{e}^*(k_2 | \tilde{\mathbf{k}} j)}{[\omega(\tilde{\mathbf{k}} j) \omega(-\tilde{\mathbf{k}} j)]^{\frac{1}{2}}} \times \\ &\quad \left[ (2n_\lambda + 1) - 12\beta \sum_{\mathbf{k}_{3j_3}} V^{(4)}(-\tilde{\mathbf{k}} j; \tilde{\mathbf{k}} j; \mathbf{k}_{3j_3}; -\mathbf{k}_{3j_3}) \times \right. \\ &\quad \left. \left\{ \frac{(2n_{\lambda_3} + 1)(2n_1 + 1)}{\beta \hbar \omega_1} \right\} + 18\beta^2 \sum_{o_{j_1'}} \sum_{k_{2'j_2'}} V^{(3)}(-\mathbf{k}_{1j_1}; \mathbf{k}_{1j_1}; o_{j_1'}) \times \right. \\ &\quad \left. V^{(3)}(o_{j_1'}; \mathbf{k}_{2'j_2'}; -\mathbf{k}_{2'j_2'}) (2n_{\lambda_2'} + 1) \cdot \frac{2(2n_1 + 1)}{\beta^2 \hbar^2 \omega_{\lambda_1} \omega_1} + \right. \\ &\quad \left. 18\beta^2 \sum_{\mathbf{k}_{2'j_2'}} \sum_{\mathbf{k}_{3'j_3'}} |V^{(3)}(\tilde{\mathbf{k}} j; \mathbf{k}_{2'j_2'}; \mathbf{k}_{3'j_3'})|^2 \sum_{n=-\infty}^{+\infty} |g(\lambda_1, i\omega_n)|^2 (\beta \hbar)^{-1} \times \right. \\ &\quad \left. \left\{ \frac{n_2 - n_3}{\omega_2 - \omega_3 - i\omega_n} + \frac{n_2 - n_3}{\omega_2 - \omega_3 + i\omega_n} - \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 - i\omega_n} - \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 + i\omega_n} \right\} \right] \quad (27) \end{aligned}$$

Further, we have

$$\begin{aligned} \langle AB \rangle &= -\frac{\hbar}{2N(M_{k_1} M_{k_2})^{\frac{1}{2}}} \sum_{\alpha} \sum_{\beta} \sum_{\tilde{\mathbf{k}}' j'} k_\alpha k_\beta \times \\ &\quad \frac{\mathbf{e}_\alpha(k_1 | \tilde{\mathbf{k}} j) \mathbf{e}_\beta(k_2 | \tilde{\mathbf{k}}' j')}{[\omega(\tilde{\mathbf{k}} j) \omega(\tilde{\mathbf{k}}' j')]^{\frac{1}{2}}} \exp[2\pi i \tilde{\mathbf{k}}' \cdot \mathbf{x}(l)] \langle A_{\tilde{\mathbf{k}} j}^-(0) A_{\tilde{\mathbf{k}}' j'}^-(\tau) \rangle \quad (28) \end{aligned}$$

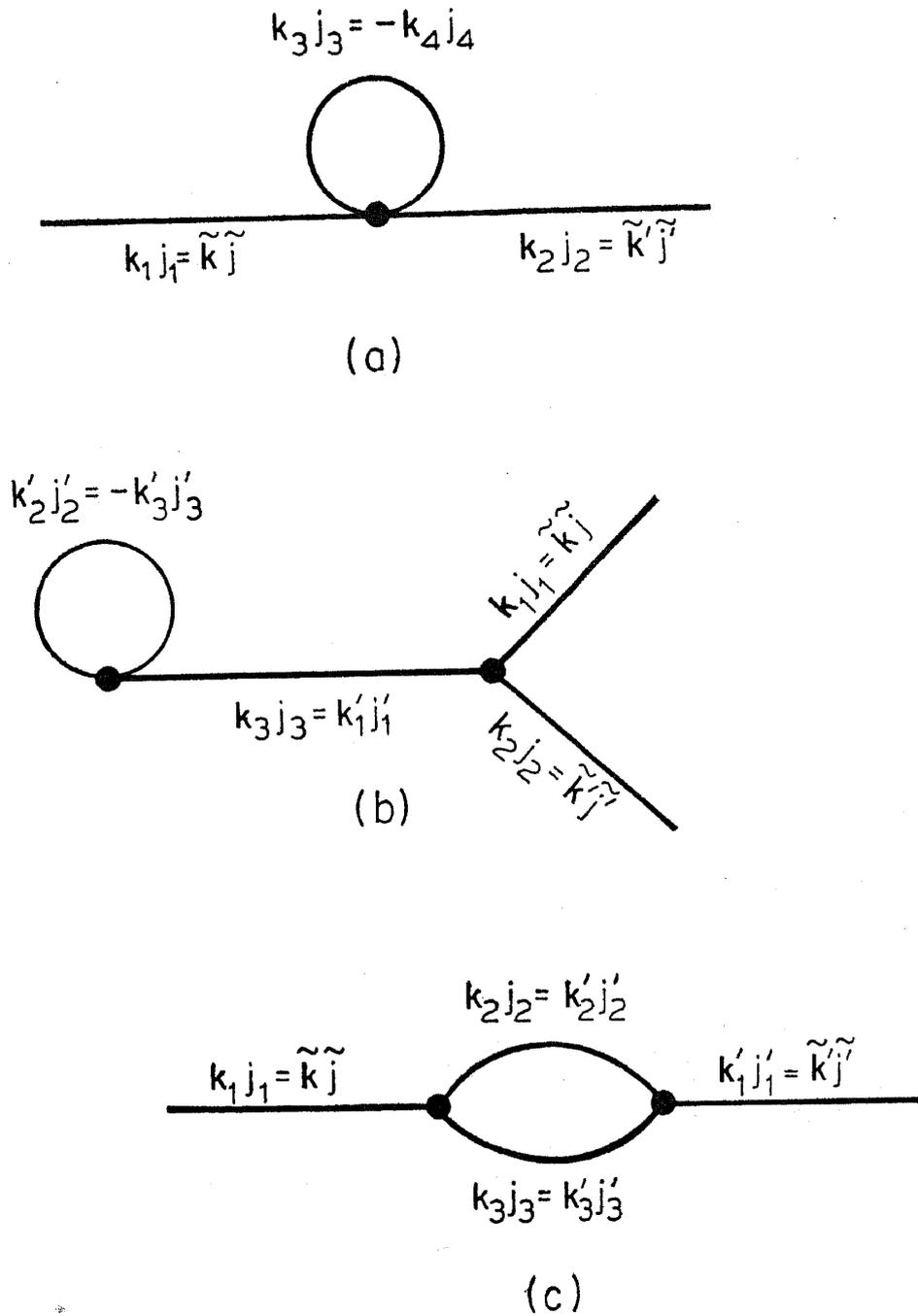


Figure 2. Diagrams that contribute to  $\langle A_{\tilde{k}\tilde{j}}(\tau_1) A_{\tilde{k}'\tilde{j}'}(\tau_2) \rangle$  type averages.

where the thermal average

$$\langle A_{\tilde{k}\tilde{j}}(0) A_{\tilde{k}'\tilde{j}'}(\tau) \rangle$$

has the following expression:

$$\langle A_{\tilde{k}\tilde{j}}(0) A_{\tilde{k}'\tilde{j}'}(\tau) \rangle = \delta_{\tilde{k}\tilde{j}, -\tilde{k}'\tilde{j}'} g(\tilde{k}\tilde{j}; \tau) -$$

(22) for the average of the product of two operators in terms of the harmonic phonon propagator, we find that

$$\begin{aligned} \langle A_{\tilde{\mathbf{k}}\tilde{j}}(\tau) A_{\tilde{\mathbf{k}}'\tilde{j}'}(\tau) A_{\tilde{\mathbf{k}}''\tilde{j}''}(\tau) \rangle &= \langle A_{\tilde{\mathbf{k}}\tilde{j}}(0) A_{\tilde{\mathbf{k}}'\tilde{j}'}(0) A_{\tilde{\mathbf{k}}''\tilde{j}''}(0) \rangle \\ &= -6\beta V^{(3)}(-\tilde{\mathbf{k}}\tilde{j}; -\tilde{\mathbf{k}}'\tilde{j}'; -\tilde{\mathbf{k}}''\tilde{j}'') \times \\ &\quad \left[ \frac{(n_1+1)(n_2+1)(n_3+1) - n_1 n_2 n_3}{\beta \hbar (\omega_1 + \omega_2 + \omega_3)} + \frac{(n_2+1)(n_3+1)n_1 - n_2 n_3 (n_1+1)}{\beta \hbar (\omega_2 + \omega_3 - \omega_1)} \right. \\ &\quad \left. + \text{two similar terms obtained by the cyclic permutation of 1, 2} \right. \\ &\quad \left. \text{and 3} \right] \end{aligned} \quad (30)$$

$$\begin{aligned} \langle A_{\tilde{\mathbf{k}}\tilde{j}}(0) A_{\tilde{\mathbf{k}}'\tilde{j}'}(\tau) A_{\tilde{\mathbf{k}}''\tilde{j}''}(\tau) \rangle &= -(6/\hbar) V^{(3)}(-\tilde{\mathbf{k}}\tilde{j}; -\tilde{\mathbf{k}}'\tilde{j}'; -\tilde{\mathbf{k}}''\tilde{j}'') \times \\ &\quad \sum_n g(\lambda, i\omega_n) \exp(i\hbar\omega_n\tau) \left[ \frac{n_2 - n_3}{\omega_2 - \omega_3 - i\omega_n} + \frac{n_2 - n_3}{\omega_2 - \omega_3 + i\omega_n} - \right. \\ &\quad \left. \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 + i\omega_n} - \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 - i\omega_n} \right] \end{aligned} \quad (31)$$

A similar expression holds good for

$$\langle A_{\tilde{\mathbf{k}}\tilde{j}}(0) A_{\tilde{\mathbf{k}}'\tilde{j}'}(0) A_{\tilde{\mathbf{k}}''\tilde{j}''}(\tau) \rangle.$$

The thermal averages  $\langle A^3 \rangle$ ,  $\langle B^3 \rangle$ ,  $\langle AB^2 \rangle$ , and  $\langle A^2 B \rangle$  depend on these expectation values and can be obtained by substituting (30) and (31) in the expansion for these operators using the formula of the type (13) for  $\mathbf{u}_\alpha \begin{pmatrix} l \\ k \end{pmatrix}$ .

#### 4. The anharmonic correction to the scattering cross-section

The previous two sections give the expectation values of all the operators that are needed to evaluate  $S(\mathbf{k}, \omega)$  as given by equations (17), (18), (27), (28), (30) and (31). From (2), it follows that the differential scattering cross-section depends on the Fourier transform of

$$\left\langle \exp \left[ -i\mathbf{k} \cdot \mathbf{u} \begin{pmatrix} 0 \\ k_1 \end{pmatrix} \right] \exp \left[ i\mathbf{k} \cdot \mathbf{u} \begin{pmatrix} l \\ k_2 \end{pmatrix} \right] \right\rangle$$

and this thermal average of the product of two operators again is given by the expansion (11). It can be seen from the previous sections that the averages  $\langle A \rangle$ ,  $\langle B \rangle$ ,  $\langle A^2 \rangle$ ,  $\langle B^2 \rangle$ ,  $\langle A^3 \rangle$ ,  $\langle B^3 \rangle$ ,  $W_A$  and  $W_B$  are independent of time and hence can be taken outside the integral sign in (2). Let us now write

$$\mathbf{R}(k_2) = \mathbf{r}(k_2) + \langle \mathbf{u}(k_2) \rangle, \quad (32)$$

$$\mathbf{R}(k_1) = \mathbf{r}(k_1) + \langle \mathbf{u}(k_1) \rangle, \quad (33)$$

$$-\tilde{W}_A = \frac{1}{2} \{ \langle A^2 \rangle - \langle A \rangle^2 \} + \frac{1}{6} [ \langle A^3 \rangle - 3 \langle A \rangle \langle A^2 \rangle + 2 \langle A \rangle^3 ], \quad (34)$$

so that  $-W_A = \langle A \rangle - \tilde{W}_A$ , (35)

$$D_{AB} = -\langle A \rangle \langle B \rangle - \frac{1}{2} \langle A^2 \rangle \langle B \rangle + \langle A \rangle^2 \langle B \rangle \\ - \frac{1}{2} \langle A \rangle \langle B^2 \rangle + \langle A \rangle \langle B^2 \rangle, \quad (36)$$

$$\alpha = 1 - \langle A \rangle - \langle B \rangle. \quad (37)$$

We could then take out all the quantities independent of time outside the time integral and we can rewrite equation (2) as

$$S(\mathbf{k}, \omega) = N \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [R(k_2) - R(k_1)]) \times \\ \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \sum_l \exp(i\mathbf{k} \cdot \mathbf{r}(l)) \times \int \exp(i\omega t) dt \times \\ \exp\{\alpha \langle AB \rangle + \frac{1}{2} \langle A^2 B \rangle + \frac{1}{2} \langle AB^2 \rangle\}. \quad (38)$$

The above equation brings out two important factors. Firstly the phase factor contributed by any atom  $k_2$  is not  $\exp[i\mathbf{k} \cdot \mathbf{r}(k_2)]$  but should be corrected by the modified position vector  $R(k_2) = \mathbf{r}(k_2) + \langle \mathbf{u}(k_2) \rangle$  including the sublattice displacement of the atom  $k_2$ . This is what one can expect on physical grounds because the position vector of an atom changes as a result of sublattice displacements when anharmonicity is switched on, and the relative sublattice displacements of two atoms contribute to the phase of the scattering and consequently to the total differential scattering cross-section by the crystal. Secondly the Debye-Waller factor  $\exp(-W_A - W_B)$  gets altered in two ways; firstly it contains the additional terms like  $\langle A^2 \rangle$  given in the square bracket of (34) and secondly it contains an additional exponential factor  $D_{AB}$  defined by (36), which involves, sublattice displacements. Thus, as the crystal is heated and anharmonicity becomes more prominent, the sublattice displacements will assume greater importance and will alter the Debye-Waller factor.

We shall next consider the integral

$$F(\omega) = \int \exp(i\omega t) dt \exp\{\alpha \langle AB \rangle + \frac{1}{2} \langle A^2 B \rangle + \frac{1}{2} \langle AB^2 \rangle\},$$

which reduces to

$$F(\omega) = \int \exp(i\omega t) dt \{1 + \alpha \langle AB \rangle + \frac{1}{2} \langle AB^2 \rangle + \frac{1}{2} \langle A^2 B \rangle \\ + \text{higher order terms}\}, \quad (39)$$

on expanding the exponential and restricting ourselves to the first term. The first integral gives rise to a  $\delta(\omega)$  factor. One can then rewrite equation (38) as

$$S(\mathbf{k}, \omega) = S^{(0)}(\mathbf{k}, \omega) + S^{(1)}(\mathbf{k}, \omega) + S^{(2)}(\mathbf{k}, \omega) \quad (40)$$

where

$$S^{(0)}(\mathbf{k}, \omega) = 2\pi N^2 \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \cdot \Delta(\mathbf{k}) \cdot \delta(\omega), \quad (41)$$

$$S^{(1)}(\mathbf{k}, \omega) = N \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times a \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \sum_l \exp(i\mathbf{k} \cdot \mathbf{r}(l)) F_{AB}(\omega), \quad (42)$$

$$S^{(2)}(\mathbf{k}, \omega) = N \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \sum_l \exp(i\mathbf{k} \cdot \mathbf{r}(l)) \left\{ \frac{1}{2} F_{AB^2}(\omega) + \frac{1}{2} F_{A^2B}(\omega) \right\}. \quad (43)$$

Here

$$F_{AB}(\omega) = \int \exp(i\omega t) dt \langle AB \rangle, \quad (44a)$$

$$F_{AB^2}(\omega) = \int \exp(i\omega t) dt \langle AB^2 \rangle, \text{ etc.} \quad (44b)$$

$S^{(0)}(\mathbf{k}, \omega)$  corresponds to the usual Bragg reflection with sharp maxima occurring whenever  $\mathbf{k}$  is a translation vector of the reciprocal lattice. Sharp peaks occur in the scattering cross-section if  $\mathbf{k}_0 = \mathbf{k}$  and  $\omega = 0$ . As stated earlier, anharmonicity affects the neutron scattering in two ways. Firstly, it introduces sublattice displacements which modify the phase factor of the scattering by any particular atom; secondly, as a result of the noncommutability of the operators as given by (11), the Debye-Waller factor gets modified by the inclusion of thermal averages of higher order operators as well as by terms involving sublattice displacements. It is clear that a study of the temperature variation of the Bragg scattering itself could give adequate information about the sublattice displacements of the atoms.

In equation (38) the operator  $B$  is a time-dependent Heisenberg operator defined in accordance with (4). In § 3 we had evaluated the expectation values of the operators  $AB$ ,  $A^2B$  and  $AB^2$  in the interaction picture, but here the time-dependence of the operators was defined in accordance with (21). Let us now write

$$f_{AB}(\tau) = \langle T A \exp(\tau H) B \exp(-\tau H) \rangle = \langle T AB(\tau) \rangle. \quad (45)$$

If the Fourier series for  $f_{AB}(\tau)$  is written in the form

$$f_{AB}(\tau) = \sum_{\nu=-\infty}^{+\infty} a_{\nu} \exp(i\hbar\omega_{\nu}\tau), \quad (46)$$

where  $\omega_{\nu} = 2\pi\nu/\beta\hbar$  (47)

where 
$$S^{(0)}(\mathbf{k}, \omega) = 2\pi N^2 \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \cdot \Delta(\mathbf{k}) \cdot \delta(\omega), \quad (41)$$

$$S^{(1)}(\mathbf{k}, \omega) = N \cdot \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times a \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \sum_l \exp(i\mathbf{k} \cdot \mathbf{r}(l)) F_{AB}(\omega), \quad (42)$$

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Here 
$$F_{AB}(\omega) = \int \exp(i\omega t) dt \langle AB \rangle, \quad (44a)$$

$$F_{AB^2}(\omega) = \int \exp(i\omega t) dt \langle AB^2 \rangle, \text{ etc.} \quad (44b)$$

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then an important result of Green's function theory asserts (Ludwig 1967, 1969) that the Fourier integral  $F_{AB}(\omega)$  is related to the Fourier coefficients  $a_\nu$  by means of the relation

$$F_{AB}(\omega) = \lim_{\epsilon \rightarrow 0} \left\{ \frac{a(-\omega + i\epsilon/\hbar) - a(-\omega - i\epsilon/\hbar)}{2\pi i \exp(-\beta\hbar\omega) - 1} \right\}, \quad (48)$$

where  $z = i\omega_\nu \rightarrow \omega + i\epsilon/\hbar$  and  $a_\nu \rightarrow a(z)$ . We make use of the above result to evaluate the integral (44a) for  $F_{AB}(\omega)$ . Due to lack of space we do not reproduce the algebraic details. One can find that the final expression for  $S^{(1)}(\mathbf{k}, \omega)$  can be expressed in the form

$$\begin{aligned} S^{(1)}(\mathbf{k}, \omega) = & -N^2 \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp(i\mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]) \times \\ & \exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \left( \frac{-\hbar}{2NM_k} \right) \sum_{\tilde{\mathbf{k}}_j} \sum_{\tilde{\mathbf{k}}'_j} \times \\ & \frac{\mathbf{k} \cdot \mathbf{e}(k_1/\tilde{\mathbf{k}}_j) \mathbf{k} \cdot \mathbf{e}(k_2/\tilde{\mathbf{k}}'_j)}{[\omega(\tilde{\mathbf{k}}_j) \omega(\tilde{\mathbf{k}}'_j)]^{1/2} (\exp(-\beta\hbar\omega) - 1)} \frac{b}{a^2 + b^2} \cdot \Delta(\mathbf{k} + 2\pi\mathbf{k}), \end{aligned} \quad (49)$$

where

$$\begin{aligned} b = & -\frac{18\pi\beta}{\hbar} \sum_{k_2 j_2} \sum_{k_3 j_3} |V^{(3)}(-\tilde{\mathbf{k}}_j; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3})|^2 \times \\ & [(n_2 - n_3) \{-\delta(\omega_2 - \omega_3 - \omega) + \delta(\omega_2 - \omega_3 + \omega)\} - \\ & (n_2 + n_3 + 1) \{-\delta(\omega_2 + \omega_3 - \omega) + \delta(\omega_2 + \omega_3 + \omega)\}], \end{aligned} \quad (50)$$

and

$$a = \frac{\beta\hbar}{2\omega_\lambda} [(\omega_\lambda + \Delta\omega_\lambda)^2 - \omega^2]. \quad (51)$$

The frequency shift  $\Delta\omega_\lambda$  in the spectral line arising from anharmonicity effects is given by

$$\begin{aligned} \Delta\omega_\lambda = & \frac{12}{\hbar} \sum_{k_3 j_3} V^{(4)}(\tilde{\mathbf{k}}_j; -\tilde{\mathbf{k}}'_j; \mathbf{k}_{3j_3}; -\mathbf{k}_{3j_3}) \times \\ & (2n_{\lambda 3} + 1) - \frac{36}{\hbar^2} \sum_{k'_{1j_1}} \sum_{k'_{2j_2}} V^{(3)}(-\tilde{\mathbf{k}}_j; -\tilde{\mathbf{k}}'_j; -\mathbf{k}'_{1j_1}) \times \\ & V^{(3)}(\mathbf{k}'_{1j_1}; \mathbf{k}'_{2j_2}; -\mathbf{k}'_{2j_2}) \left( \frac{2n_{\lambda' 2} + 1}{\omega_{\lambda' 1}} \right) \\ & - \frac{18}{\hbar^2} \sum_{k_2 j_2} \sum_{k_3 j_3} |V^{(3)}(-\tilde{\mathbf{k}}_j; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3})|^2 \cdot \left\{ \frac{n_2 - n_3}{\omega_2 - \omega_3 - \omega} \right. \\ & \left. + \frac{n_2 - n_3}{\omega_2 - \omega_3 + \omega} - \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 - \omega} - \frac{n_2 + n_3 + 1}{\omega_2 + \omega_3 + \omega} \right\}. \end{aligned} \quad (52)$$

This expression agrees with the expression for the line shift given by Maradudin and Fein (1962), Kokkeedee (1962) and Cowley (1963, 1968) with the exception of the second term involving

$$V^{(3)}(\mathbf{k}'_{j1}; \mathbf{k}'_{j2}; -\mathbf{k}'_{j2'})$$

which was not considered in their work. Normally the contribution of these terms can be expected to be negligible, but if the mode  $\lambda_1'$  happens to be a soft mode as for ferroelectric crystals,  $\omega_{\lambda_1'}$  will be very small near the phase transition and the interaction with the soft mode can be an important source of contribution to the line width and shift of spectral lines for ferroelectric crystals.

The expression for  $b$  gives the width of the spectral lines which account for the finite life time of the phonons and it agrees with the expression given by Maradudin and Fein, Kokkeedee, and Cowley. The formula (49) brings out the well-known fact that anharmonicity will shift the spectral lines as well as give them a finite width, and instead of a delta function which one might obtain in the harmonic approximation, one gets a Lorentzian form for the absorption or emission cross-section in one phonon processes.

### 5. Evaluation of $F_{AB^2}(\omega)$ and $F_{A^2B}(\omega)$

Next, the integrals for  $F_{AB^2}(\omega)$  and  $F_{A^2B}(\omega)$  defined by equation (44) can be evaluated by the same method adopted for  $F_{AB}(\omega)$ . We give only the final results which are given by

$$F_{AB^2}(\omega) = \frac{-i\hbar^{3/2}}{(2N)^{3/2} M_{k_1}^{1/2} M_{k_2}} \sum_{\tilde{\mathbf{k}}_j} \sum_{\tilde{\mathbf{k}}'_j} \sum_{\tilde{\mathbf{k}}''_j} \frac{\mathbf{k} \cdot \mathbf{e}(k_1 | \tilde{\mathbf{k}}_j) \mathbf{k} \cdot \mathbf{e}(k_2 | \tilde{\mathbf{k}}'_j) \mathbf{k} \cdot \mathbf{e}(k_2 | \tilde{\mathbf{k}}''_j)}{[\omega(\tilde{\mathbf{k}}_j) \omega(\tilde{\mathbf{k}}'_j) \omega(\tilde{\mathbf{k}}''_j)]^{1/2} [\exp(-\beta\hbar\omega) - 1]} \cdot V^{(3)}(-\tilde{\mathbf{k}}_j; -\tilde{\mathbf{k}}'_j; -\tilde{\mathbf{k}}''_j) \times$$

$$\left( \frac{-24\omega_1}{\beta\hbar^2} \right) [(n_2 - n_3) (\omega_2 - \omega_3) \text{Sgn } x \cdot \delta \{(\omega_1^2 - \omega^2) [(\omega_2 - \omega_3)^2 - \omega^2]\} - (n_2 + n_3 + 1) (\omega_2 + \omega_3) \text{Sgn } y \cdot \delta \{(\omega_1^2 - \omega^2) [(\omega_2 + \omega_3)^2 - \omega^2]\}] \quad (53)$$

$$\text{where } \left. \begin{aligned} x &= (\omega_1^2 - \omega^2) + (\omega_2 - \omega_3)^2 - \omega^2 \\ y &= (\omega_1^2 - \omega^2) + (\omega_2 + \omega_3)^2 - \omega^2 \end{aligned} \right\} \quad (54)$$

Similarly we find that

$$F_{A^2B}(\omega) = \frac{i\hbar^{3/2}}{(2N)^{3/2} M_{k_1} M_{k_2}^{1/2}} \sum_{\tilde{\mathbf{k}}_j} \sum_{\tilde{\mathbf{k}}'_j} \sum_{\tilde{\mathbf{k}}''_j}$$

$$\frac{k.e(k_1 | \tilde{\mathbf{k}}_j) k.e(k_1 | \tilde{\mathbf{k}}'_{j'}) k.e(k_2 | \tilde{\mathbf{k}}''_{j''})}{[\omega(\tilde{\mathbf{k}}_j) \omega(\tilde{\mathbf{k}}'_{j'}) \omega(\tilde{\mathbf{k}}''_{j''})]^{1/2} (\exp(-\beta\hbar\omega) - 1)} \cdot V^{(3)}(-\tilde{\mathbf{k}}_j; -\tilde{\mathbf{k}}'_{j'}; -\tilde{\mathbf{k}}''_{j''}) \times$$

$$\left( -\frac{24\omega_3}{\beta\hbar^2} \right) [(n_1 - n_2) (\omega_1 - \omega_2) \text{Sgn } x' \cdot \delta((\omega_3^2 - \omega^2) [(\omega_1 - \omega_2)^2 - \omega^2])$$

$$- (n_1 + n_2 + 1) (\omega_1 + \omega_2) \text{Sgn } y' \cdot \delta((\omega_3^2 - \omega^2) [(\omega_1 + \omega_2)^2 - \omega^2])], \quad (55)$$

where

$$\left. \begin{aligned} x' &= (\omega_3^2 - \omega^2) + (\omega_1 - \omega_2)^2 - \omega^2 \\ y' &= (\omega_3^2 - \omega^2) + (\omega_1 + \omega_2)^2 - \omega^2 \end{aligned} \right\}. \quad (56)$$

One may notice that the expressions for  $F_{AB^2}(\omega)$  and  $F_{A^2B}(\omega)$  are different from each other in three ways. Firstly, the sign is different and this is because the sign of the operators  $A$  and  $B$  as defined by (9) and (10) are different. Secondly, the frequency  $\omega_3 = \omega(\tilde{\mathbf{k}}''_{j''})$  corresponding to the operator  $A_{\tilde{\mathbf{k}}''_{j''}}(\tau)$  which has a different time from the operators  $A_{\tilde{\mathbf{k}}_j}(0)$  and  $A_{\tilde{\mathbf{k}}'_{j'}}(0)$ , occurs as a factor in (55) as well as in the delta term as a factor  $(\omega_3^2 - \omega^2)$  but the combination in  $F_{AB^2}(\omega)$  is the factors  $\omega_1$  and  $\delta(\omega_1^2 - \omega^2)$ . This is because the operator  $A_{\tilde{\mathbf{k}}_j}(0)$  has a different time from the other two operators  $A_{\tilde{\mathbf{k}}'_{j'}}(\tau)$  and  $A_{\tilde{\mathbf{k}}''_{j''}}(\tau)$ . Thirdly, the mass factors occurring in the denominator in the two expressions are different.

The expression for  $S^{(2)}(\mathbf{k}_1, \omega)$  thus becomes

$$S^{(2)}(\mathbf{k}, \omega) = \frac{N^2}{2} \sum_{k_1 k_2} f_{k_1}^* f_{k_2} \exp\{i \mathbf{k} \cdot [\mathbf{R}(k_2) - \mathbf{R}(k_1)]\}$$

$$\exp(-\tilde{W}_A - \tilde{W}_B + D_{AB}) \cdot \Delta(\mathbf{k}) [F_{AB^2}(\omega) + F_{A^2B}(\omega)]. \quad (57)$$

The above expression involves two-phonon processes and the delta factor in  $F_{AB^2}(\omega)$  is nonzero whenever  $\omega = \omega_1$  or  $\omega = \omega_2 \pm \omega_3$ . Similarly the delta factor in  $F_{A^2B}(\omega)$  is nonzero whenever  $\omega = \omega_3$  or  $\omega = \omega_1 \pm \omega_2$ . It may be noticed that while  $F_{AB}(\omega)$  which gives the linewidth and shift involves terms of the order  $[V^{(3)}]^2$  or  $V^{(4)}$ , the above term which depends on quantum effects emerging from the noncommutability of the operators in the presence of anharmonicity depends only on

$$V^{(3)}(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'').$$

This term represents the interference between the one-phonon peak and the diffuse multiphonon background, and was found to be small by Maradudin and Ambegaokar (1964) who evaluated this term in an integral form. We have given in (53) and (55) an explicit expression for this interference term.

## 6. Evaluation of the third order elastic constants of cubic crystals from Neutron scattering data

In this section we suggest a method to evaluate the third order elastic (TOE) constants of cubic crystals from the experimental measurements on the width of the spectral

lines. Equation (50) gives the expression for the width of the spectral lines observed in elastic coherent neutron scattering.

Under an elastic deformation, the displacement of an atom of the crystal is given by

$$\mathbf{u}_a(l) = \mathbf{u}_a(k) + \sum_{\beta} u_{a\beta} \mathbf{x}_{\beta}(l), \quad (58)$$

where  $u_{a\beta}$  are the strain constants and  $u_a(k)$  denotes the inner displacement of the atom  $k$ . The inner displacements are linear functions of the strain coefficients and thus (58) suggests that the displacement of any atom in a crystal is a linear function of the strain coefficients. Substituting (58) in the second order potential energy of the crystal, one can obtain the deformation energy of the lattice as a quadratic in the strain coefficients. Similarly substituting (58) in the third order terms of the vibrational potential energy of the lattice, we can obtain a cubic expression in the strain coefficients. Let the strain coefficients be denoted by  $e_{xy}$  so that

$$e_{xy} = \frac{1}{2} (u_{xy} + u_{yx}) = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right). \quad (59)$$

The third order deformation energy can then be expressed as

$$V^{(3)} = \sum_{xy} \sum_{x'y'} \sum_{x''y''} C_{xy, x'y', x''y''} e_{xy} e_{x'y'} e_{x''y''}. \quad (60)$$

If we establish a correspondence between the letter pairs ( $xx, yy, zz, yz, zx, xy$ ) and the numbers (1, 2, 3, 4, 5, 6), the expression for  $V^{(3)}$  reduces to

$$V^{(3)} = \sum_i \sum_j \sum_k C_{ijk} \eta_i \eta_j \eta_k, \quad (61)$$

where  $\eta_i = e_{xy}$  if  $i$  stands for the pair  $xy$  etc. The  $C_{ijk}$  are the TOE constants and the above expression for  $V^{(3)}$  is the third order deformation energy of a crystal.  $V^{(3)}$  is invariant under symmetry operations of the lattice.

Our aim is to outline a method of evaluating the TOE constants from neutron scattering data. We shall consider simple cubic Bravais lattices only. The third order terms of the anharmonic Hamiltonian of a crystal are given by (Born and Huang 1954).

$$H_A = \frac{1}{6\sqrt{N}} \sum_{\mathbf{k}j} \sum_{\mathbf{k}'j'} \sum_{\mathbf{k}''j''} \Delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \phi(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \times \\ Q(\mathbf{k}j) Q(\mathbf{k}'j') Q(\mathbf{k}''j''), \quad (62)$$

where  $Q(\mathbf{k}j)$  denotes a normal co-ordinate of the lattice. The displacement of an atom of the crystal is (Maradudin *et al* 1971).

$$u_a(l) = \frac{1}{\sqrt{NM}} \sum_{\mathbf{k}j} e_x(\mathbf{k}j) \exp[(2\pi i \mathbf{k} \cdot \mathbf{x}(l)] Q(\mathbf{k}j). \quad (63)$$

Thus the thermal strains may be expressed as

$$e_{xy} = \frac{\pi i}{\sqrt{NM}} \sum_{\mathbf{k}_j} \exp [2\pi i \mathbf{k} \cdot \mathbf{x}(l)] \mathcal{L}_{xy}(\mathbf{k}_j) Q(\mathbf{k}_j) \quad (64)$$

where  $\mathcal{L}_{xy}(\mathbf{k}_j) = k_y e_x(\mathbf{k}_j) + k_x e_y(\mathbf{k}_j)$  (65)

Substituting these in (60) and substituting the resulting equation in

$$H_A = V \sum_l V^{(3)}, \quad (66)$$

we obtain

$$H_A = \frac{(\pi i)^3}{N^{1/2} M^{3/2}} V \sum_{\mathbf{k}_j} \sum_{\mathbf{k}'_{j'}} \sum_{\mathbf{k}''_{j''}} \sum_{xy} \sum_{x'y'} \sum_{x''y''} C_{xy, x'y', x''y''} \times \\ \Delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \mathcal{L}_{xy}(\mathbf{k}_j) \mathcal{L}_{x'y'}(\mathbf{k}'_{j'}) \mathcal{L}_{x''y''}(\mathbf{k}''_{j''}) Q(\mathbf{k}_j) Q(\mathbf{k}'_{j'}) Q(\mathbf{k}''_{j''}) \quad (67)$$

where  $V$  is the unit cell volume. Comparing (67) with (62) we arrive at

$$\phi(\mathbf{k}_j; \mathbf{k}'_{j'}; \mathbf{k}''_{j''}) = \frac{6(\pi i)^3}{M^{1/2}} V \sum_{\mathbf{k}_j} \sum_{\mathbf{k}'_{j'}} \sum_{\mathbf{k}''_{j''}} \sum_{xy} \sum_{x'y'} \sum_{x''y''} \\ C_{xy, x'y', x''y''} \mathcal{L}_{xy}(\mathbf{k}_j) \mathcal{L}_{x'y'}(\mathbf{k}'_{j'}) \mathcal{L}_{x''y''}(\mathbf{k}''_{j''}). \quad (68)$$

This expression gives the anharmonicity coefficient connecting the lattice modes  $\mathbf{k}_j$ ,  $\mathbf{k}'_{j'}$  and  $\mathbf{k}''_{j''}$  with the TOE constants for a Bravais lattice.

The third order anharmonicity constants are given by (Maradudin and Fein 1962)

$$V^{(3)}(\mathbf{k}_{1j_1}; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3}) = \frac{\hbar^{3/2}}{2^{3/2} 6 \sqrt{N}} \frac{\Delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \phi(\mathbf{k}_{1j_1}; \mathbf{k}_{2j_2}; \mathbf{k}_{3j_3})}{[\omega(\mathbf{k}_{1j_1}) \omega(\mathbf{k}_{2j_2}) \omega(\mathbf{k}_{3j_3})]^{1/2}}. \quad (69)$$

Substituting (68) and (69) in (50) and simplifying, the expression for the phonon linewidth is obtained as

$$b(\mathbf{k}_j) = \frac{9}{4} \frac{\pi^3 \beta \hbar^2 V^2}{M} \sum_{\mathbf{k}_{2j_2}} \sum_{\mathbf{k}_{3j_3}} \frac{\Delta(\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k})}{\omega(-\mathbf{k}_j) \omega(\mathbf{k}_{2j_2}) \omega(\mathbf{k}_{3j_3})} \times \\ \sum_{xy} \sum_{x'y'} \sum_{x''y''} \sum_{\tilde{x}\tilde{y}} \sum_{\tilde{x}'\tilde{y}'} \sum_{\tilde{x}''\tilde{y}''} C_{xy, x'y', x''y''} C_{\tilde{x}\tilde{y}, \tilde{x}'\tilde{y}', \tilde{x}''\tilde{y}''} \times \\ \mathcal{L}_{xy}(-\mathbf{k}_j) \mathcal{L}_{x'y'}(\mathbf{k}_{2j_2}) \mathcal{L}_{x''y''}(\mathbf{k}_{3j_3}) \mathcal{L}_{\tilde{x}\tilde{y}}(-\mathbf{k}_j) \mathcal{L}_{\tilde{x}'\tilde{y}'}(\mathbf{k}_{2j_2}) \times \\ \mathcal{L}_{\tilde{x}''\tilde{y}''}(\mathbf{k}_{3j_3}) [(n_2 - n_3) \{-\delta(\omega_2 - \omega_3 - \omega) + \delta(\omega_2 - \omega_3 + \omega)\} \\ - (n_2 + n_3 + 1) \{-\delta(\omega_2 + \omega_3 - \omega) + \delta(\omega_2 + \omega_3 + \omega)\}]. \quad (70)$$

Consider the product

$$P_{xy, \tilde{x}\tilde{y}}(\mathbf{k}_{2j_2}, \mathbf{k}_{3j_3}) = \sum_{x'y'} \sum_{x''y''} \sum_{\tilde{x}'\tilde{y}'} \sum_{\tilde{x}''\tilde{y}''} C_{xy, x'y', x''y''} \times \\ C_{\tilde{x}\tilde{y}, \tilde{x}'\tilde{y}', \tilde{x}''\tilde{y}''} \cdot \mathcal{L}_{x'y'}(\mathbf{k}_{2j_2}) \mathcal{L}_{x''y''}(\mathbf{k}_{3j_3}) \mathcal{L}_{\tilde{x}'\tilde{y}'}(\mathbf{k}_{2j_2}) \mathcal{L}_{\tilde{x}''\tilde{y}''}(\mathbf{k}_{3j_3})$$

This becomes

$$P_{xy, \tilde{x}\tilde{y}}(\mathbf{k}_{2j_2}, \mathbf{k}_{3j_3}) = 16 \sum_{x'y'} \sum_{x''y''} \sum_{\tilde{x}'\tilde{y}'} \sum_{\tilde{x}''\tilde{y}''} C_{xy, x'y', x''y''} \times \\ C_{\tilde{x}\tilde{y}, \tilde{x}'\tilde{y}', \tilde{x}''\tilde{y}''} \cdot k_{2y'} e_{x'} k_{3y''} e_{x''} k_{2\tilde{y}'} e_{\tilde{x}'} k_{3\tilde{y}''} e_{\tilde{x}''} \quad (71)$$

in view of the relation (65). In the above we have the relation  $\mathbf{k}_3 = \mathbf{k} - \mathbf{k}_2$ . Then (70) can be rewritten as

$$b(\mathbf{k}_j) = \frac{9}{4} \frac{\pi^2 \beta \hbar^2 V^2}{M} \sum_{\mathbf{k}_{2j_2}} \sum_{j_3} \sum_{xy} \sum_{\tilde{x}\tilde{y}} \\ \frac{P_{xy, \tilde{x}\tilde{y}}(\mathbf{k}_{2j_2}, \mathbf{k}_{3j_3})}{\omega(-\mathbf{k}_j) \omega(\mathbf{k}_{2j_2}) \omega(\mathbf{k}_{3j_3})} \mathcal{L}_{xy}(-\mathbf{k}_j) \mathcal{L}_{\tilde{x}\tilde{y}}(-\mathbf{k}_j) \times \\ [(n_2 - n_3) \{-\delta(\omega_2 - \omega_3 - \omega) + \delta(\omega_2 - \omega_3 + \omega)\}] \\ - (n_2 + n_3 + 1) \{-\delta(\omega_2 + \omega_3 - \omega) + \delta(\omega_2 + \omega_3 + \omega)\}], \quad (72)$$

where  $\omega_2 = \omega(\mathbf{k}_{2j_2})$  and  $\omega_3 = \omega(\mathbf{k}_{3j_3}) = \omega(\mathbf{k} - \mathbf{k}_{2j_2})$ .

We will use the convention that all the frequencies are positive. If for any particular value of  $\mathbf{k}_2$ , the relation  $\omega(\mathbf{k}_{2j_2}) - \omega(\mathbf{k}_2 - \mathbf{k}, j) = \omega(\mathbf{k}_j)$  is satisfied, then the first delta factor will contribute to the sum in (72). Let us denote the corresponding value of  $\mathbf{k}_2$  by  $\mathbf{K}_2^{(1)}$ . If  $-\omega(\mathbf{k}_{2j_2}) + \omega(-\mathbf{k}_2 + \mathbf{k}, j)$  is positive and is equal to  $\omega(\mathbf{k}_j)$ , we denote the corresponding value of  $\mathbf{k}_2$  by  $\mathbf{K}_2^{(2)}$ . Similarly the value of  $\mathbf{k}_2$  for which the relation  $\omega(\mathbf{k}_j) = \omega(\mathbf{k}_{2j_2}) + \omega(\mathbf{k} - \mathbf{k}_2, j)$  is satisfied, will be noted by the symbol  $\mathbf{K}_2^{(3)}$ .  $\mathbf{K}_2^{(1)}$ ,  $\mathbf{K}_2^{(2)}$  and  $\mathbf{K}_2^{(3)}$  can be evaluated by solving the lattice dynamical dispersion equation for the crystal. Let us write

$$\left. \begin{aligned} n_2^{(i)} &= n[\omega(\mathbf{K}_2^{(i)}, j_2) \text{ and} \\ n_3^{(i)} &= n[\omega(-\mathbf{K}_2^{(i)} + \mathbf{k}, j_3)], \quad i = 1, 2, 3 \end{aligned} \right\} \quad (73)$$

On evaluating the contributions from the delta factors, we have

$$b(\mathbf{k}_j) = \frac{9}{4} \frac{\pi^3 \beta \hbar^2 V^2}{M} \sum_{j_2 j_3} \sum_{xy} \sum_{\tilde{x}\tilde{y}} P_{xy, \tilde{x}\tilde{y}}(j_2 j_3) \times$$

$$\frac{\mathcal{L}_{xy}(-\mathbf{k}_j) \mathcal{L}_{\tilde{x}\tilde{y}}(-\mathbf{k}_j)}{\omega(-\mathbf{k}_j) \omega(\mathbf{k}_{2j_2}) \omega(\mathbf{k}_{3j_3})} \{-n [\omega(\mathbf{K}_2^{(1)}, j_2)]$$

$$+ n [\omega(-\mathbf{K}_2^{(1)} + \mathbf{k}, j_3)] + n [\omega(\mathbf{K}_2^{(2)}, j_2)] - n [\omega(\mathbf{k} - \mathbf{K}_2^{(2)}, j_3)]$$

$$- n [\omega(\mathbf{K}_2^{(1)}, j_2)] - n [\omega(\mathbf{k} - \mathbf{K}_2^{(3)}, j_3)] - 1\}. \quad (74)$$

Also we get

$$\sum_{xy} \sum_{\tilde{x}\tilde{y}} P_{xy, \tilde{x}\tilde{y}}(j_2 j_3) \mathcal{L}_{xy}(-\mathbf{k}_j) \mathcal{L}_{\tilde{x}\tilde{y}}(-\mathbf{k}_j) =$$

$$4 \sum_{xy} \sum_{\tilde{x}\tilde{y}} P_{xy, \tilde{x}\tilde{y}}(j_2 j_3) e_x k_y e_{\tilde{x}} k_{\tilde{y}} =$$

$$64 \sum_{xy} \sum_{x'y'} \sum_{x''y''} \sum_{\tilde{x}\tilde{y}} \sum_{\tilde{x}'\tilde{y}'} \sum_{\tilde{x}''\tilde{y}''} C_{xy, x'y', x''y''} C_{\tilde{x}\tilde{y}, \tilde{x}'\tilde{y}', \tilde{x}''\tilde{y}''} \times$$

$$e_x k_y e_{\tilde{x}} k_{\tilde{y}} k_{2y'} e_{x'} k_{3y''} e_{x''} k_{2\tilde{y}'} e_{\tilde{x}'} k_{3\tilde{y}''} e_{\tilde{x}''}. \quad (75)$$

For a cubic crystal, the above expression is a quadratic in the six TOE constants  $C_{111}$ ,  $C_{112}$ ,  $C_{144}$ ,  $C_{166}$ ,  $C_{123}$  and  $C_{456}$ . One can evaluate the coefficients of all the 21 products. For example, the coefficient of  $C_{111}^2$  in the above expression is

$$64 \sum_x k_{2x}^2 k_{3x}^2 e_x^4$$

and the coefficient of  $C_{112}^2$  is

$$\sum k_{2x}^2 k_{3y}^2 e_x^2 e_y^2$$

where the sum is over the three values  $x, y, z$  for the components of  $\mathbf{k}$  or  $\mathbf{e}$ . Similarly, one can evaluate the coefficients of all the 21 coefficients  $C_{xyz} C_{x'y'z'}$  in the sum (75). If one finds out from lattice dynamical calculations the vectors  $\mathbf{K}_2^{(1)}$ ,  $\mathbf{K}_2^{(2)}$  and  $\mathbf{K}_2^{(3)}$ , the right hand side of the expression for  $b(\mathbf{k}_j)$  which is a quadratic in the six TOE constants of a cubic crystal, can be determined. If one uses 21 distinct values of  $b(\mathbf{k}_j)$  obtained from neutron scattering experiments, the 21 product terms of the type  $C_{xyz} C_{x'y'z'}$  can be obtained directly by matrix inversion and the TOE constants can be evaluated from these products. But even this is not necessary as the right hand side of (75) depends only on the six independent TOE constants. One can evaluate by a process of iteration all the six TOE constants if the experimental value of  $b(\mathbf{k}_j)$  are known for six distinct values of  $b(\mathbf{k}_j)$ . Thus neutron scattering data on the width of the spectral lines could provide a powerful method for evaluating the third order elastic constants of cubic Bravais lattices.

## References

- Barron T H K and Klein M L 1974 in *Dynamical properties of solids* eds G K Horton and A A Maradudin (Amsterdam: North Holland Pub. Co.) Vol 1
- Born M and Huang K 1954 *Dynamical theory of crystal lattices* (London: Oxford Pub. House)
- Blink R and Zeks B 1974 *Soft modes in ferroelectrics and antiferroelectrics* (Amsterdam: North Holland Pub. Co.)
- Cowley R A 1963 *Adv. Phys.* **12** 461
- Cowley R A 1968 *Rep. Prog. Phys.* **31** 123
- Kokkedee J J J 1962 *Physica* **28** 374
- Ludwig W 1967 in *Springer tracts in modern physics* ed G Höhler (Berlin: Springer Verlag) Vol. 43
- Ludwig W 1967 in *Elementary excitations in solids* eds A A Maradudin and G F Nardelli (New York: Plenum)
- Maradudin A A and Ambegaokar V 1964 *Phys. Rev.* **135** A1071
- Maradudin A A and Fein A E 1962 *Phys. Rev.* **128** 2589
- Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 *Theory of Lattice dynamics in the harmonic approximation. Solid State Phys. Suppl.* (New York: Academic Press) Vol. 3
- Thompson B V 1963 *Phys. Rev.* **131** 1420
- Viswanathan K S and Watanabe K 1966 *Phys. Rev.* **149** 614