

where  $c_\xi$  is the relative abundance of the  $\xi$ th isotope,  $I_\xi$  its nuclear spin, and  $b_\xi^+$  and  $b_\xi^-$  its scattering lengths. The quantity  $\bar{b}$  is known as the *coherent* scattering length of the element or nuclide. It is conventional to quote the values of  $\bar{b}$  and  $\bar{b}^2$  in terms of the two quantities  $\sigma_{\text{coh}}$  and  $\sigma_{\text{inc}}$  defined in (2.70). A list of the values of  $\sigma_{\text{coh}}$  and  $\sigma_{\text{inc}}$  for the elements, together with a description of the methods of measuring these quantities, has been given by Koester (1977). A few of the values are given in Table 2.1.

Table 2.1 Values of  $\sigma_{\text{coh}}$  and  $\sigma_{\text{inc}}$ 

Element or nuclide	Z	$\sigma_{\text{coh}}$	$\sigma_{\text{inc}}$	Element	Z	$\sigma_{\text{coh}}$	$\sigma_{\text{inc}}$
$^1\text{H}$	1	1.8	80.2	V	23	0.02	5.0
$^2\text{H}$	1	5.6	2.0	Fe	26	11.5	0.4
C	6	5.6	0.0	Co	27	1.0	5.2
O	8	4.2	0.0	Ni	28	13.4	5.0
Mg	12	3.6	0.1	Cu	29	7.5	0.5
Al	13	1.5	0.0	Zn	30	4.1	0.1

The units of  $\sigma_{\text{coh}}$  and  $\sigma_{\text{inc}}$  are  $10^{-28} \text{ m}^2$ . The values are taken from Koester (1977).

The extension of the theory to scattering systems containing more than one element is readily made. If for example the scattering system is a crystal of NaCl, the coherent scattering is that due to a hypothetical crystal in which all the sodium nuclei have scattering lengths equal to  $\bar{b}$  for sodium, and all the chlorine nuclei have scattering lengths equal to  $\bar{b}$  for chlorine. The incoherent scattering is the sum of the incoherent scattering from the sodium nuclei and the incoherent scattering from the chlorine nuclei.

## Nuclear scattering by crystals

### 3.1 Introduction

In the present chapter we evaluate the cross-sections when the scattering system is a single crystal. We start by considering a Bravais crystal, i.e. a crystal with one atom per unit cell. Denote the sides of the unit cell by  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  (see Fig. 3.1). Then a lattice vector is given by

$$\mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3, \quad (3.1)$$

where  $l_1$ ,  $l_2$ ,  $l_3$  are integers. The volume of the unit cell is

$$v_0 = \mathbf{a}_1 \cdot [\mathbf{a}_2 \times \mathbf{a}_3]. \quad (3.2)$$

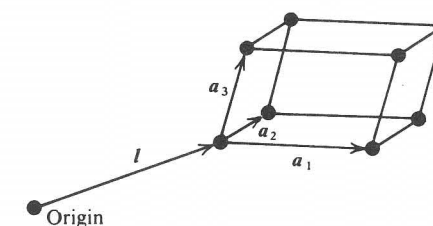
We define the reciprocal lattice to be a lattice with unit-cell vectors  $\boldsymbol{\tau}_1$ ,  $\boldsymbol{\tau}_2$ ,  $\boldsymbol{\tau}_3$ , where

$$\begin{aligned} \boldsymbol{\tau}_1 &= \frac{2\pi}{v_0} [\mathbf{a}_2 \times \mathbf{a}_3], & \boldsymbol{\tau}_2 &= \frac{2\pi}{v_0} [\mathbf{a}_3 \times \mathbf{a}_1], \\ \boldsymbol{\tau}_3 &= \frac{2\pi}{v_0} [\mathbf{a}_1 \times \mathbf{a}_2]. \end{aligned} \quad (3.3)$$

The volume of the unit cell in the reciprocal lattice is

$$\boldsymbol{\tau}_1 \cdot [\boldsymbol{\tau}_2 \times \boldsymbol{\tau}_3] = \frac{(2\pi)^3}{v_0}. \quad (3.4)$$

Fig. 3.1 Unit cell of crystal.



From (3.3)  $\mathbf{a}_i \cdot \boldsymbol{\tau}_j = 2\pi\delta_{ij}$ . (3.5)

Owing to thermal motion the nucleus  $l$  is displaced from its equilibrium position  $\mathbf{l}$ . Its instantaneous position is

$$\mathbf{R}_l = \mathbf{l} + \mathbf{u}_l, \quad (3.6)$$

where  $\mathbf{u}_l$  is the displacement from the equilibrium position (Fig. 3.2). The index  $j$  with which we previously labelled a nucleus now becomes  $l$ .

For a Bravais crystal the correlation between the positions of the nuclei  $l$  and  $l'$  depends only on  $l - l'$ . So in (2.68), for each value of  $l'$ , the sum over  $l$  is the same. We may thus put  $l' = 0$ . Similarly in (2.69) each term in  $l$  is the same and equal to the term  $l = 0$ . Therefore

$$\begin{aligned} \sum_{ll'} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{l'}(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_l(t)\} \rangle \\ = N \sum_l \langle \exp\{i\boldsymbol{\kappa} \cdot \mathbf{l}\} \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{u}_l(t)\} \rangle, \end{aligned} \quad (3.7)$$

$$\begin{aligned} \sum_l \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_l(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_l(t)\} \rangle \\ = N \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{u}_0(t)\} \rangle, \end{aligned} \quad (3.8)$$

where  $N$  is the number of nuclei in the crystal.  $\mathbf{u}_l(t)$  is the Heisenberg operator for  $\mathbf{u}_l$ . In these equations we have used the relation

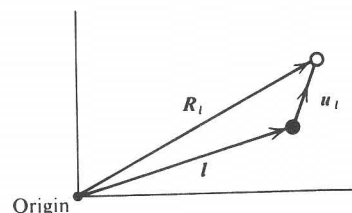
$$\mathbf{R}_l(t) = \mathbf{l} + \mathbf{u}_l(t), \quad (3.9)$$

which follows from (3.6), since  $\mathbf{l}$  is a constant.

### 3.2 Normal modes

We assume that the interatomic forces in the crystal are harmonic, i.e. that the forces are linear functions of the displacements. For such forces the displacements  $\mathbf{u}_l$  can be expressed as the sum of displace-

Fig. 3.2 Position of nucleus  $l$ : ● equilibrium position, ○ actual (instantaneous) position.



ments due to a set of normal modes. Thus

$$\mathbf{u}_l = \left( \frac{\hbar}{2MN} \right)^{1/2} \sum_s \frac{\mathbf{e}_s}{\omega_s} \{ a_s \exp(i\mathbf{q} \cdot \mathbf{l}) + a_s^\dagger \exp(-i\mathbf{q} \cdot \mathbf{l}) \}, \quad (3.10)$$

where  $\mathbf{q}$  is the wavevector of the mode, and  $j$  is its polarisation index ( $j = 1, 2, 3$ ).  $s$  stands for the double index  $\mathbf{q}, j$ .  $\omega_s$  is the angular frequency of mode  $s$ , and  $\mathbf{e}_s$  is its polarisation vector. The sum over  $s$  is over the  $N$  values of  $\mathbf{q}$  in the 1st Brillouin zone, and over the three values of  $j$ .  $M$  is the mass of an atom – assumed to be the same for all the atoms.  $a_s$  is the annihilation operator for the mode  $s$ , and  $a_s^\dagger$ , its Hermitian conjugate, is the creation operator. These operators are discussed in Appendix E. Normal modes are discussed in Appendix G, where (3.10) is derived.

$\mathbf{u}_l(t)$  is obtained from (3.10) by replacing  $a_s$  and  $a_s^\dagger$  by their Heisenberg operators,  $a_s(t)$  and  $a_s^\dagger(t)$ . It is shown in Appendix E.1 that

$$a_s(t) = \exp(iHt/\hbar) a_s \exp(-iHt/\hbar) = a_s \exp(-i\omega_s t), \quad (3.11)$$

$$a_s^\dagger(t) = \exp(iHt/\hbar) a_s^\dagger \exp(-iHt/\hbar) = a_s^\dagger \exp(i\omega_s t). \quad (3.12)$$

Thus

$$\begin{aligned} \boldsymbol{\kappa} \cdot \mathbf{u}_l(t) = \left( \frac{\hbar}{2MN} \right)^{1/2} \sum_s \frac{\boldsymbol{\kappa} \cdot \mathbf{e}_s}{\omega_s} [a_s \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\} \\ + a_s^\dagger \exp\{-i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\}]. \end{aligned} \quad (3.13)$$

### 3.3 Probability function for a harmonic oscillator

The theory of the scattering of thermal neutrons by crystals is much simplified by the use of a result, first derived by Bloch (1932), for the probability function of a harmonic oscillator.

We first define the probability function for a single bound particle – not necessarily a harmonic oscillator – moving in one dimension. Denote the displacement or position variable by  $Q$ . Denote the Hamiltonian by  $H$ , and its normalised eigenfunctions and eigenvalues by  $\psi_n$  and  $E_n$ . Then

$$H\psi_n = E_n\psi_n. \quad (3.14)$$

If the particle is in an energy eigenstate  $n$ , the probability of finding the displacement between  $Q$  and  $Q + dQ$  is  $|\psi_n(Q)|^2 dQ$ . Suppose the particle is not in a single state  $n$ , but in an incoherent mixture of states. If the particle is a member of an ensemble of similar particles

at temperature  $T$ , the probability of its being in the state  $n$  is

$$p_n = \frac{1}{Z} \exp(-E_n \beta), \quad Z = \sum_n \exp(-E_n \beta), \quad \beta = \frac{1}{k_B T}. \quad (3.15)$$

We define the probability function  $f(Q)$  by

$$f(Q) = \sum_n p_n |\psi_n(Q)|^2. \quad (3.16)$$

$f(Q) dQ$  is the probability of finding the displacement between  $Q$  and  $Q + dQ$ . Since the  $\psi_n$  are normalised, and  $\sum_n p_n = 1$ , it follows from (3.16) that

$$\int_{-\infty}^{\infty} f(Q) dQ = 1, \quad (3.17)$$

a necessary result in view of the probability significance of  $f(Q)$ .

We can express  $\langle A(Q) \rangle$ , the thermal average of a function  $A(Q)$ , in terms of  $f(Q)$ . From (2.58)

$$\begin{aligned} \langle A(Q) \rangle &= \sum_n p_n \int_{-\infty}^{\infty} A(Q) |\psi_n(Q)|^2 dQ \\ &= \int_{-\infty}^{\infty} A(Q) \sum_n p_n |\psi_n(Q)|^2 dQ \\ &= \int_{-\infty}^{\infty} A(Q) f(Q) dQ. \end{aligned} \quad (3.18)$$

Bloch showed that, for a one-dimensional harmonic oscillator, the probability function is a Gaussian, given by

$$f(Q) = C \exp(-Q^2/2\sigma^2), \quad (3.19)$$

$$\text{where} \quad \sigma^2 = \frac{\hbar}{2M\omega} \coth(\frac{1}{2}\hbar\omega\beta). \quad (3.20)$$

$M$  is the mass of the particle, and  $\omega$  the angular frequency.  $C$  is a normalising constant obtained from (3.17). It follows from (3.18) and (3.19) that the thermal averages of  $\exp Q$  and  $Q^2$  are related by

$$\langle \exp Q \rangle = \exp\{\frac{1}{2}\langle Q^2 \rangle\}. \quad (3.21)$$

The results (3.19) to (3.21) are derived in Appendix E.2.

### 3.4 Development of $\langle \exp U \exp V \rangle$

We first evaluate the coherent cross-section. From (2.68) and (3.7)

$$\begin{aligned} \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \sum_i \exp(i\mathbf{\kappa} \cdot \mathbf{l}) \int_{-\infty}^{\infty} \langle \exp U \exp V \rangle \\ &\quad \times \exp(-i\omega t) dt, \end{aligned} \quad (3.22)$$

where

$$U = -i\mathbf{\kappa} \cdot \mathbf{u}_0(0) = -i \sum_s g_s a_s + g_s a_s^+, \quad (3.23)$$

$$V = i\mathbf{\kappa} \cdot \mathbf{u}_l(t) = i \sum_s h_s a_s + h_s^* a_s^+, \quad (3.24)$$

$$g_s = \left( \frac{\hbar}{2MN} \right)^{1/2} \frac{\mathbf{\kappa} \cdot \mathbf{e}_s}{\sqrt{\omega_s}}, \quad (3.25)$$

$$h_s = \left( \frac{\hbar}{2MN} \right)^{1/2} \frac{\mathbf{\kappa} \cdot \mathbf{e}_s}{\sqrt{\omega_s}} \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\}. \quad (3.26)$$

Eqs. (3.23) to (3.26) follow from (3.13).

We now develop the expression  $\langle \exp U \exp V \rangle$ . In addition to the result that the probability function for a harmonic oscillator is a Gaussian, we need the following results:

(i) The  $a$  and  $a^+$  operators for different oscillators commute. For the same oscillator, the commutation relation for  $a$  and  $a^+$  is given by (E.8). The two results are combined in the equation

$$[a_s, a_{s'}^+] = \delta_{ss'}. \quad (3.27)$$

(ii) If  $A$  and  $B$  are any two operators whose commutator is a  $c$ -number (i.e. a number as opposed to an operator), then

$$\exp A \exp B = \exp(A+B) \exp\{\frac{1}{2}(AB-BA)\}. \quad (3.28)$$

This result is proved in Appendix I.1.

We first prove that  $UV - VU$  is a  $c$ -number. From (3.23) and (3.24)

$$\begin{aligned} UV - VU &= \sum_s (g_s a_s + g_s a_s^+) \sum_{s'} (h_{s'} a_{s'} + h_{s'}^* a_{s'}^+) \\ &\quad - \sum_{s'} (h_{s'} a_{s'} + h_{s'}^* a_{s'}^+) \sum_s (g_s a_s + g_s a_s^+). \end{aligned} \quad (3.29)$$

Eq. (3.27) shows that all the terms on the right-hand side of (3.29) give zero, except those with  $s' = s$ . Thus

$$\begin{aligned} UV - VU &= \sum_s (g_s h_s^* - g_s h_s) (a_s a_s^+ - a_s^+ a_s) \\ &= \sum_s (g_s h_s^* - g_s h_s), \end{aligned} \quad (3.30)$$

which is a  $c$ -number.

We next use (3.28) for the operators  $U$  and  $V$ , and take the thermal average

$$\langle \exp U \exp V \rangle = \langle \exp(U+V) \rangle \exp\{\frac{1}{2}(UV - VU)\}. \quad (3.31)$$

Note that the second term on the right-hand side is a number that does not depend on  $T$ . The quantity  $U + V$  is a linear combination of

harmonic displacements. Each displacement has a Gaussian probability function. The probability function for a linear combination of Gaussians is itself a Gaussian. We can therefore apply (3.21) to  $U + V$ .

$$\langle \exp(U + V) \rangle = \exp\{\frac{1}{2}\langle (U + V)^2 \rangle\}. \quad (3.32)$$

From (3.31) and (3.32)

$$\begin{aligned} \langle \exp U \exp V \rangle &= \exp\{\frac{1}{2}\langle (U + V)^2 \rangle\} \exp\{\frac{1}{2}\langle UV - VU \rangle\} \\ &= \exp\{\frac{1}{2}\langle U^2 + V^2 + UV + VU + UV - VU \rangle\} \\ &= \exp\{\frac{1}{2}\langle U^2 + V^2 \rangle\} \exp\langle UV \rangle. \end{aligned} \quad (3.33)$$

Now

$$\langle U^2 \rangle = \langle V^2 \rangle. \quad (3.34)$$

This can be proved formally, but it can be seen on physical grounds.  $U$  is proportional to the component in the direction of  $\kappa$  of the displacement of the origin atom at time zero.  $V$  is the corresponding quantity – apart from a change of sign – for the atom  $l$  at time  $t$ . But the zero of time is arbitrary, and for a Bravais crystal all the atoms are equivalent. So the average values of  $U^2$  and  $V^2$  are equal.

From (3.33) and (3.34)

$$\langle \exp U \exp V \rangle = \exp\langle U^2 \rangle \exp\langle UV \rangle. \quad (3.35)$$

This completes the development of  $\langle \exp U \exp V \rangle$ . Substituting (3.35) in (3.22) gives

$$\begin{aligned} \left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{\text{coh}} &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \exp\langle U^2 \rangle \sum_l \exp(i\kappa \cdot l) \\ &\quad \times \int_{-\infty}^{\infty} \exp\langle UV \rangle \exp(-i\omega t) dt. \end{aligned} \quad (3.36)$$

### 3.5 Phonon expansion

A crystal of  $N$  atoms has  $3N$  normal modes. The initial state  $\lambda$  of the crystal is given by specifying  $n_1, n_2, \dots, n_{3N}$ , the quantum numbers of the  $3N$  oscillators corresponding to the normal modes. In a general scattering process, the state of the crystal changes to  $\lambda'$ , which is given by another set of quantum numbers  $n'_1, n'_2, \dots, n'_{3N}$ . The scattering process may be classified according to the changes in the quantum numbers.

*Elastic process.* All the quantum numbers remain unchanged, i.e.

$$n'_i = n_i \quad (3.37)$$

for all  $i$  from 1 to  $3N$ .

*One-phonon process.* All the quantum numbers remain unchanged except for one, that of oscillator  $\alpha$ , which changes by unity, i.e.

$$\begin{aligned} n'_i &= n_i, \quad \text{all } i \text{ except } \alpha, \\ n'_\alpha &= n_\alpha \pm 1. \end{aligned} \quad (3.38)$$

*Two-phonon process.* All the quantum numbers remain unchanged except for two, those of oscillators  $\alpha$  and  $\beta$ , which change by unity, i.e.

$$\begin{aligned} n'_i &= n_i, \quad \text{all } i \text{ except } \alpha \text{ and } \beta, \\ n'_\alpha &= n_\alpha \pm 1, \quad n'_\beta = n_\beta \pm 1. \end{aligned} \quad (3.39)$$

Similarly for three, four, etc. phonon processes.

If we expand the term  $\exp\langle UV \rangle$  in (3.36)

$$\exp\langle UV \rangle = 1 + \langle UV \rangle + \frac{1}{2!} \langle UV \rangle^2 + \dots + \frac{1}{p!} \langle UV \rangle^p + \dots, \quad (3.40)$$

then the  $p$ th term gives the cross-section for all  $p$ -phonon processes. Thus the first term, 1, gives the elastic cross-section. The next term  $\langle UV \rangle$  gives the cross-section for all one-phonon processes in which  $\alpha$  is in turn each of the numbers 1 to  $3N$ , and, for each  $\alpha$ ,  $n_\alpha$  either increases or decreases by unity. The term  $(1/2!)\langle UV \rangle^2$  gives the cross-section for all two-phonon processes in which the combination  $\alpha, \beta$  is in turn each of the  $3N(3N-1)/2$  combinations of two oscillators selected from  $3N$ , and, for each combination,  $n_\alpha$  and  $n_\beta$  increase or decrease by unity. And so on.

The statement that the  $p$ th term in the expansion of  $\exp\langle UV \rangle$  corresponds to a  $p$ -phonon process can be justified in two ways. One way is to go back to expression (2.49) for the cross-section for a specific  $\lambda \rightarrow \lambda'$  transition. Instead of summing over all  $\lambda'$ , sum only over those  $\lambda'$  which, for a fixed  $\lambda$ , correspond to a  $p$ -phonon process. Then average over  $\lambda$  as before. The result, after a somewhat lengthy calculation, is the expression in (3.36) with  $\exp\langle UV \rangle$  replaced by  $(1/p!)\langle UV \rangle^p$ . The second way is simply to inspect the expressions for each term. They contain  $\delta$ -functions which show that the process is elastic, one-phonon, two-phonon, and so on. This is the line we shall follow.



### 3.6 Coherent elastic scattering

#### Bragg's law

Replace  $\exp(UV)$  by 1 in (3.36)

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \exp\langle U^2 \rangle \sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}) \int_{-\infty}^{\infty} \exp(-i\omega t) dt. \quad (3.41)$$

The integral with respect to  $t$  is

$$\int_{-\infty}^{\infty} \exp(-i\omega t) dt = 2\pi\delta(\omega) = 2\pi\hbar\delta(\hbar\omega) \quad (3.42)$$

(see Appendix A.2). Since  $\hbar\omega$  is the change in the energy of the neutron we see that the scattering is elastic. Thus

$$|\mathbf{k}'| = |\mathbf{k}|, \quad (3.43)$$

and (3.41) becomes

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} N \exp\langle U^2 \rangle \sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}) \delta(\hbar\omega). \quad (3.44)$$

We can immediately integrate with respect to  $E'$  to obtain the differential scattering cross-section  $d\sigma/d\Omega$ . The energy  $E$  of the incident neutrons is fixed. Therefore

$$dE' = -d(\hbar\omega), \quad (3.45)$$

and we have

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{\text{coh el}} &= \int_0^\infty \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh el}} dE' \\ &= \frac{\sigma_{\text{coh}}}{4\pi} N \exp\langle U^2 \rangle \sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}). \end{aligned} \quad (3.46)$$

The lattice sum can be written in the form (see Appendix A.4)

$$\sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}) = \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{\kappa} - \boldsymbol{\tau}), \quad (3.47)$$

where  $v_0$  is the volume of the unit cell of the crystal, and  $\boldsymbol{\tau}$  is a vector in the reciprocal lattice. Thus

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} N \frac{(2\pi)^3}{v_0} \exp(-2W) \sum_{\boldsymbol{\tau}} \delta(\mathbf{\kappa} - \boldsymbol{\tau}), \quad (3.48)$$

where

$$2W = -\langle U^2 \rangle = \langle \{\mathbf{\kappa} \cdot \mathbf{u}_0(0)\}^2 \rangle. \quad (3.49)$$

Eq. (3.48) tells us that the scattering occurs only when

$$\mathbf{\kappa} = \mathbf{k} - \mathbf{k}' = \boldsymbol{\tau}. \quad (3.50)$$

This condition is the same as Bragg's law for X-ray scattering. So coherent elastic scattering of neutrons is simply Bragg scattering.

We can represent (3.50) by a diagram in reciprocal space. Fig. 3.3 shows the reciprocal lattice with the origin at  $O$ .  $AO$  represents the wavevector of the incident neutrons, and  $AB$  that of the scattered neutrons. Since the scattering is elastic,  $AO = AB$ . In general the point  $B$  does not coincide with a reciprocal lattice point, and there is no coherent elastic scattering (Fig. 3.3a). But for special orientations of  $\mathbf{k}$  with respect to the crystal lattice (and hence to the reciprocal lattice), and for special scattering angles  $\theta$ ,  $B$  can coincide with a reciprocal lattice point (Fig. 3.3b). Coherent scattering then occurs. In Fig. 3.3b,  $OAB$  is an isosceles triangle with  $BO = \boldsymbol{\tau}$ . Thus

$$\tau = 2k \sin \frac{1}{2}\theta. \quad (3.51)$$

The vector  $\boldsymbol{\tau}$  is perpendicular to a set of crystal planes. Its magnitude is

$$\tau = n \frac{2\pi}{d}, \quad (3.52)$$

where  $d$  is the spacing of the planes, and  $n$  is an integer. Also

$$k = \frac{2\pi}{\lambda}, \quad (3.53)$$

where  $\lambda$  is the wavelength of the neutrons. Substituting these relations in (3.51) gives

$$n\lambda = 2d \sin \frac{1}{2}\theta, \quad (3.54)$$

which is the familiar form of Bragg's law.

Fig. 3.3 Bragg's law in reciprocal space. (a)  $\mathbf{\kappa} \neq \boldsymbol{\tau}$ ; no coherent elastic scattering. (b)  $\mathbf{\kappa} = \boldsymbol{\tau}$ ; coherent elastic scattering occurs.

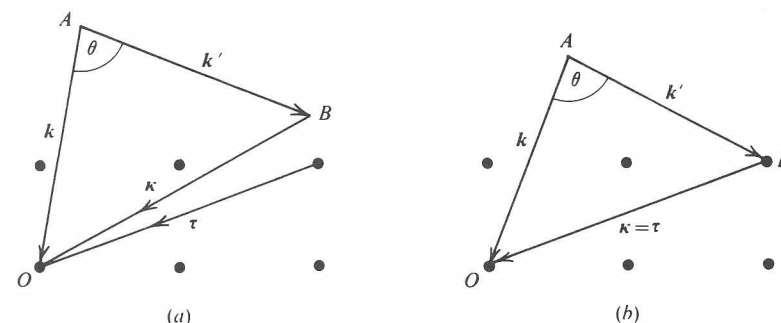


Fig. 3.3b is more usually drawn as in Fig. 3.4, which shows the crystal planes acting as a mirror for the incident and reflected neutrons. It can be seen that  $\frac{1}{2}\theta$  is the angle between  $\mathbf{k}$  and the crystal planes.

### Debye-Waller factor

The exponential term in (3.48) is known as the *Debye-Waller factor*. From (3.23)

$$\begin{aligned} 2W &= -\langle U^2 \rangle = \sum_{\lambda} p_{\lambda} \sum_{ss'} g_s g_{s'} \langle \lambda | (a_s + a_s^+)(a_{s'} + a_{s'}^+) | \lambda \rangle \\ &= \sum_{\lambda} p_{\lambda} \sum_s g_s^2 \langle \lambda | a_s a_s^+ + a_s^+ a_s | \lambda \rangle. \end{aligned} \quad (3.55)$$

The last step follows because the matrix elements are zero except for terms with  $a_s a_s^+$  and  $a_s^+ a_s$  (see Appendix E.1). From (E.13)

$$\langle \lambda | a_s a_s^+ + a_s^+ a_s | \lambda \rangle = 2n_s + 1, \quad (3.56)$$

where  $n_s$  is the quantum number of the  $s$ th oscillator for the state  $\lambda$ . The form of  $p_{\lambda}$  in (2.51) shows that, in averaging over  $\lambda$ , each term in the sum over  $s$  may be averaged independently. Thus from (3.25)

$$2W = \frac{\hbar}{2MN} \sum_s \frac{(\boldsymbol{\kappa} \cdot \mathbf{e}_s)^2}{\omega_s} \langle 2n_s + 1 \rangle. \quad (3.57)$$

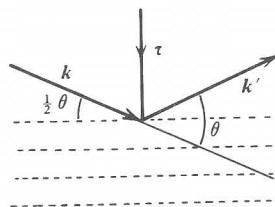
It is shown in Appendix E.3 that

$$\langle 2n_s + 1 \rangle = \coth(\frac{1}{2}\hbar\omega_s\beta), \quad (3.58)$$

whence 
$$2W = \frac{\hbar}{2MN} \sum_s \frac{(\boldsymbol{\kappa} \cdot \mathbf{e}_s)^2}{\omega_s} \coth(\frac{1}{2}\hbar\omega_s\beta). \quad (3.59)$$

*Cubic crystal.* For a cubic crystal this expression can be developed further. If, for the same polarisation branch, we sum over all the  $q$  points related by symmetry,  $\omega_s$  remains the same, and the mean value

Fig. 3.4 Relation of  $\mathbf{k}$  and  $\mathbf{k}'$  to the planes of atoms (dashed lines) in Bragg scattering.



of  $(\boldsymbol{\kappa} \cdot \mathbf{e}_s)^2$  is  $\frac{1}{3}\kappa^2$ . Thus

$$2W = \frac{\hbar}{2MN} \frac{\kappa^2}{3} \sum_s \frac{1}{\omega_s} \coth(\frac{1}{2}\hbar\omega_s\beta). \quad (3.60)$$

This result may be expressed another way. For a Bravais crystal the mean-square displacement of an atom is independent of the lattice site. We may therefore write

$$2W = \langle (\boldsymbol{\kappa} \cdot \mathbf{u})^2 \rangle = \kappa^2 \langle u_{\kappa}^2 \rangle, \quad (3.61)$$

where  $u_{\kappa}$  is the component of  $\mathbf{u}$  in the direction of  $\boldsymbol{\kappa}$ . This equation is true for any crystal. In general the quantity  $\langle u_{\kappa}^2 \rangle$  depends on the direction of  $\boldsymbol{\kappa}$ , but we can see from (3.60) that for a cubic crystal it is independent of direction. If  $u_x, u_y, u_z$  are the components of  $\mathbf{u}$  along three orthogonal directions, it follows that for a cubic crystal

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle = \frac{1}{3} \langle u^2 \rangle, \quad (3.62)$$

where  $\langle u^2 \rangle$  is the mean value of  $u^2$ . Thus

$$2W = \frac{1}{3} \kappa^2 \langle u^2 \rangle. \quad (3.63)$$

Since, for a cubic crystal, the Debye-Waller factor depends only on the frequencies of the normal modes and not on the polarisation vectors, it can be expressed in terms of  $Z(\omega)$ , the phonon density of states. The definition of this function is that  $Z(\omega) d\omega$  is the fraction of the normal modes whose frequencies lie in the range  $\omega$  to  $\omega + d\omega$ . So

$$\int_0^{\omega_m} Z(\omega) d\omega = 1, \quad (3.64)$$

where  $\omega_m$  is the maximum frequency of the normal modes. The total number of normal modes is  $3N$ . We can therefore put

$$\sum_s \frac{1}{\omega_s} \coth(\frac{1}{2}\hbar\omega_s\beta) = 3N \int_0^{\omega_m} \frac{1}{\omega} \coth(\frac{1}{2}\hbar\omega\beta) Z(\omega) d\omega. \quad (3.65)$$

Thus from (3.60)

$$2W = \frac{\hbar\kappa^2}{2M} \int_0^{\omega_m} \frac{1}{\omega} \coth(\frac{1}{2}\hbar\omega\beta) Z(\omega) d\omega. \quad (3.66)$$

and from (3.63)

$$\langle u^2 \rangle = \frac{3\hbar}{2M} \int_0^{\omega_m} \frac{1}{\omega} \coth(\frac{1}{2}\hbar\omega\beta) Z(\omega) d\omega. \quad (3.67)$$

Even for a non-cubic crystal the value of  $(\boldsymbol{\kappa} \cdot \mathbf{e}_s)^2$ , averaged over the normal modes with the same value of  $\omega_s$ , is often close to  $\frac{1}{3}\kappa^2$ , in which case the above formulae for  $2W$  and  $\langle u^2 \rangle$  are still approximately correct.

### Non-Bravais crystals

We consider coherent elastic scattering from a non-Bravais crystal, i.e. a crystal with more than one atom per unit cell. Let the equilibrium position of the  $d$ th atom in the unit cell be  $\mathbf{d}$ . The position of atom  $d$  in unit cell  $l$  is

$$\mathbf{R}_{ld} = \mathbf{l} + \mathbf{d} + \mathbf{u}_d^{(l)}, \quad (3.68)$$

where  $\mathbf{l} + \mathbf{d}$  is the equilibrium position of the atom, and  $\mathbf{u}_d^{(l)}$  is the displacement from equilibrium (Fig. 3.5). In general there is a different type of nucleus at each  $d$  position. So the mean value of the scattering length (i.e. the average over isotopes and nuclear spin) is different for each  $d$  position. Denote it by  $\bar{b}_d$ . We return to (2.68). The factor

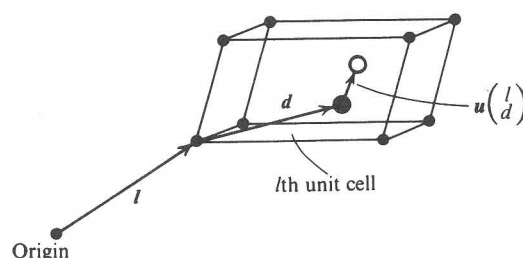
$$\frac{\sigma_{\text{coh}}}{4\pi} = (\bar{b})^2 \quad (3.69)$$

must now be taken inside the double sum over the atoms. With (3.68) the equation becomes

$$\begin{aligned} & \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} \\ &= \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{ld} \sum_{l'd'} \bar{b}_d \bar{b}_{d'} \exp\{i\boldsymbol{\kappa} \cdot (\mathbf{l} + \mathbf{d} - \mathbf{l}' - \mathbf{d}')\} \\ & \quad \times \int_{-\infty}^{\infty} \left\langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{u}_{d'}^{(l')}(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{u}_d^{(l)}(t)\} \right\rangle \exp(-i\omega t) dt. \end{aligned} \quad (3.70)$$

This is the coherent cross-section for all processes, elastic and inelastic.

Fig. 3.5 Position vectors of the atom  $l, d$  for a non-Bravais crystal: ● equilibrium position, ○ actual (instantaneous) position.



The analysis then proceeds as for the Bravais crystal and gives the result (corresponding to 3.46)

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{coh el}} = N \sum_l \exp(i\boldsymbol{\kappa} \cdot \mathbf{l}) \left| \sum_d \bar{b}_d \exp(i\boldsymbol{\kappa} \cdot \mathbf{d}) \exp(-W_d) \right|^2, \quad (3.71)$$

where 
$$W_d = \frac{1}{2} \left\langle \left\{ \boldsymbol{\kappa} \cdot \mathbf{u}_d^{(l)} \right\}^2 \right\rangle. \quad (3.72)$$

As before the quantity  $\mathbf{u}_d^{(l)}$  is expressed in terms of the displacements due to a set of normal modes. The equation corresponding to (3.10) is†

$$\mathbf{u}_d^{(l)} = \left( \frac{\hbar}{2M_d N} \right)^{1/2} \sum_s \frac{1}{\sqrt{\omega_s}} \{ e_{ds} a_s \exp(i\mathbf{q} \cdot \mathbf{l}) + e_{ds}^* a_s^\dagger \exp(-i\mathbf{q} \cdot \mathbf{l}) \}. \quad (3.73)$$

$N$  is the number of unit cells in the crystal, and  $M_d$  is the mass of the atom at position  $d$ . As before  $s$  stands for the double index  $\mathbf{q}, j$ .  $e_{ds}$  is the polarisation vector for the atom at position  $d$  for the mode  $s$ . The polarisation index  $j$  takes values 1 to  $3r$ , where  $r$  is the number of atoms per unit cell. The development of  $W_d$  is similar to the Bravais case and leads to

$$W_d = \frac{\hbar}{4M_d N} \sum_s \frac{|\boldsymbol{\kappa} \cdot \mathbf{e}_{ds}|^2}{\omega_s} \langle 2n_s + 1 \rangle. \quad (3.74)$$

In (3.71) the sum over  $l$  is carried out as before and gives

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{coh el}} = N \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}) |F_N(\boldsymbol{\kappa})|^2, \quad (3.75)$$

where 
$$F_N(\boldsymbol{\kappa}) = \sum_d \bar{b}_d \exp(i\boldsymbol{\kappa} \cdot \mathbf{d}) \exp(-W_d). \quad (3.76)$$

$F_N(\boldsymbol{\kappa})$  is known as the *nuclear unit-cell structure factor*.

### Methods of measuring Bragg scattering

The  $\delta$ -function is an elegant and powerful tool for working with highly peaked functions, but the expressions in (3.48) and (3.75) need some manipulation before they can be compared directly with the results of an actual measurement of coherent elastic scattering. In such a measurement we determine the intensity of a Bragg peak, i.e.

† The normal modes of a non-Bravais crystal are discussed in Appendix G. See also Ghatak and Kothari (1972), Appendix C.

the integrated number of neutrons as, by varying some experimental parameter, we pass through the condition  $\kappa = \tau$ . Owing to instrumental resolution and mosaic spread in the crystal, the  $\delta$ -function in the theoretical cross-section is spread out into a peak with finite width. We shall assume that the collimation of the incident and scattered neutrons is always sufficiently relaxed for all the neutrons scattered into the Bragg peak to be counted. The quantity actually measured is therefore the total cross-section  $\sigma_{\text{tot}}$  (see Section 1.3).

To calculate  $\sigma_{\text{tot}}$  we have to integrate  $d\sigma/d\Omega$  with respect to  $\Omega$  over all directions in space, i.e.

$$\sigma_{\text{tot}} = \int_{\text{all directions}} \left( \frac{d\sigma}{d\Omega} \right)_{\text{coh el}} d\Omega. \quad (3.77)$$

Consider the case where neutrons of wavevector  $k$  are incident on a crystal, so that the angle  $\psi$  between  $k$  and a specific reciprocal lattice vector  $\tau$  is fixed (Fig. 3.6). Put

$$\rho = k - \tau. \quad (3.78)$$

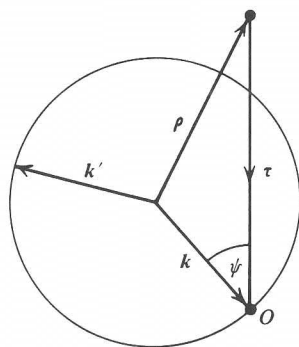
Then  $\rho$  is also fixed, and

$$\rho^2 = k^2 + \tau^2 - 2k\tau \cos \psi. \quad (3.79)$$

The integration in (3.77) is over all directions of  $k'$ , with  $k'$  fixed and equal to  $k$ , i.e. over the sphere shown in Fig. 3.6. We need consider only the  $\delta$ -function term in (3.75), i.e.

$$\int \delta(\kappa - \tau) d\Omega = \int \delta(\rho - k') d\Omega. \quad (3.80)$$

Fig. 3.6 Integration of the function  $\delta(\kappa - \tau)$  over all directions of  $k'$  in Bragg scattering.



The integral is zero unless  $\rho = k'$ , so it can be written as

$$\int \delta(\rho - k') d\Omega = c \delta(\rho^2 - k'^2). \quad (3.81)$$

The value of the constant  $c$  is obtained as follows. We note that  $\delta(\rho - k')$  is a 3-dimensional  $\delta$ -function, i.e.

$$\int \delta(\rho - k') dk' = 1, \quad (3.82)$$

where the integral is taken over all  $k'$  space. Now

$$\begin{aligned} \int \delta(\rho - k') dk' &= \int \delta(\rho - k') d\Omega k'^2 dk' \\ &= \frac{1}{2}c \int \delta(\rho^2 - k'^2) k' d(k'^2) = \frac{1}{2}c\rho. \end{aligned} \quad (3.83)$$

Therefore 
$$c = \frac{2}{\rho}, \quad (3.84)$$

whence 
$$\int \delta(\kappa - \tau) d\Omega = \frac{2}{\rho} \delta(\rho^2 - k'^2) = \frac{2}{\rho} \delta(\rho^2 - k^2). \quad (3.85)$$

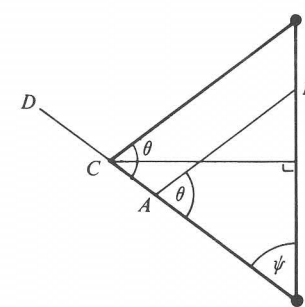
From (3.75), (3.77), (3.79), and (3.85)

$$\sigma_{\text{tot } \tau} = N \frac{(2\pi)^3}{v_0} \frac{2}{\rho} |F_N(\tau)|^2 \delta(\tau^2 - 2k\tau \cos \psi). \quad (3.86)$$

We now calculate the intensity of the Bragg peak for three standard methods, originally devised for the scattering of X-rays.

*Laue method.* Neutrons in a fixed direction ( $DO$  in Fig. 3.7), but with a continuous range of wavelengths, are incident on a crystal of fixed orientation. The angle between the scattered neutrons and the

Fig. 3.7 Diagram for the Laue method.  $AB = AO$ ,  $CT = CO$ .



incident direction is set to the value

$$\theta = \pi - 2\psi. \quad (3.87)$$

For a general value of  $k$  ( $AO$  in Fig. 3.7) there is no Bragg scattering. The wavevector of the scattered neutrons is  $AB$ , and  $BO$  ( $\kappa$ ) does not equal  $TO$  ( $\tau$ ). But for the particular value

$$k = \frac{\tau}{2 \cos \psi}, \quad (3.88)$$

represented by  $CO$  in Fig. 3.7,  $\kappa$  is equal to  $\tau$ , and the Bragg condition is satisfied. The incident neutrons contain a continuous range of  $k$  values, but only the particular value given in (3.88) appears in the scattered beam. This is a standard method of obtaining neutrons with a single  $k$  value.

Let the flux of incident neutrons with wavelengths between  $\lambda$  and  $\lambda + d\lambda$  be  $\phi(\lambda) d\lambda$ . Then the intensity for the peak corresponding to  $\tau$ , i.e. the number of neutrons per second in the scattered beam, is

$$P = \int \phi(\lambda) \sigma_{\text{tot} \tau} d\lambda \\ = N \frac{(2\pi)^3}{v_0} |F_N(\tau)|^2 \int \frac{2}{\rho} \delta(\tau^2 - 2k\tau \cos \psi) \phi(\lambda) d\lambda. \quad (3.89)$$

Change the variable of integration to

$$x = 2k\tau \cos \psi. \quad (3.90)$$

Then, since

$$\lambda = \frac{2\pi}{k}, \quad (3.91)$$

$$d\lambda = -\frac{2\pi}{k^2} dk = -\frac{2\pi}{k^2} \frac{dx}{2\tau \cos \psi}. \quad (3.92)$$

As usual, when an integrand contains a  $\delta$ -function the remaining terms are evaluated at values for which the argument of the  $\delta$ -function is zero. We therefore put

$$\rho = k, \quad \tau = 2k \cos \psi, \quad (3.93)$$

and obtain the result

$$P = N \frac{(2\pi)^3}{v_0} \frac{\pi \phi(\lambda) |F_N(\tau)|^2}{k^4 \cos^2 \psi} \\ = \frac{V}{v_0^2} \phi(\lambda) \frac{\lambda^4}{2 \sin^2 \frac{1}{2}\theta} |F_N(\tau)|^2, \quad (3.94)$$

where  $V = Nv_0$  is the volume of the crystal. The value of  $\lambda$  to be inserted in (3.94) is that of the scattered neutrons.

*Rotation of crystal.* In this method of measuring a Bragg peak, a monochromatic beam of neutrons of wavevector  $k$  is incident on a crystal that can be rotated. The scattering angle  $\theta$  is set to satisfy the relation

$$\tau = 2k \sin \frac{1}{2}\theta. \quad (3.95)$$

The crystal is rotated about an axis perpendicular to the plane containing  $k$  and  $k'$ , so that the reciprocal lattice vector  $\tau$  remains in that plane.

Let  $k$ ,  $k'$  and  $\tau$  be represented by  $AO$ ,  $AB$  and  $TO$  respectively (Fig. 3.8). As the crystal is rotated, i.e. as the angle  $\psi$  between  $k$  and  $\tau$  is varied, the point  $T$  traces out a circle, and Bragg scattering occurs as  $T$  passes through  $B$ . We again assume that, although  $\theta$  is nominally fixed, the instrumental range of  $\theta$  is sufficiently large for all the scattered neutrons to be counted as  $\psi$  is varied. The counting rate as a function of  $\psi$  is known as a *rocking curve*.

If  $\Phi$  is the flux of the incident neutrons, the integrated number of scattered neutrons per unit time in the Bragg peak is

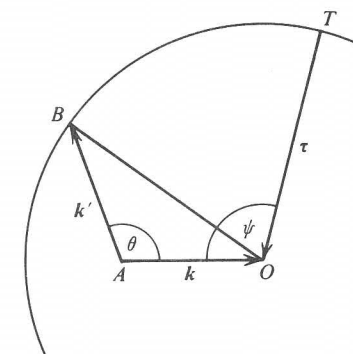
$$P = \Phi \int_0^\pi \sigma_{\text{tot} \tau} d\psi \\ = N \frac{(2\pi)^3}{v_0} \Phi |F_N(\tau)|^2 \int_0^\pi \frac{2}{\rho} \delta(\tau^2 - 2k\tau \cos \psi) d\psi. \quad (3.96)$$

$$\text{Put } x = 2k\tau \cos \psi, \quad \text{with } dx = -2k\tau \sin \psi d\psi. \quad (3.97)$$

The integral is evaluated, again with the relations in (3.93), giving the result

$$P = N \frac{(2\pi)^3}{v_0} \Phi |F_N(\tau)|^2 / Q, \quad (3.98)$$

Fig. 3.8 Diagram for the method of crystal rotation.



where  $Q = k^2 \tau \sin \psi = k^3 \sin 2\psi = k^3 \sin \theta$ . (3.99)

Thus  $P = \frac{V}{v_0^2} \Phi \frac{\lambda^3}{\sin \theta} |F_N(\tau)|^2$ , (3.100)

where  $\lambda$  is the wavelength of the incident neutrons.

We are often interested, not in the absolute intensity of a Bragg peak, but in the relative intensity of two different Bragg peaks in the same crystal. If  $P_1$  and  $P_2$  are the intensities of peaks for reciprocal lattice vectors  $\tau_1$  and  $\tau_2$ , and  $\theta_1$  and  $\theta_2$  are the corresponding scattering angles, then

$$\frac{P_1}{P_2} = \frac{|F_N(\tau_1)|^2 / \sin \theta_1}{|F_N(\tau_2)|^2 / \sin \theta_2}. \quad (3.101)$$

It may be noted that to observe a Bragg peak corresponding to a particular  $\tau$ , the value of  $k$  must be greater than  $\frac{1}{2}\tau$ , otherwise (3.95) cannot be satisfied.

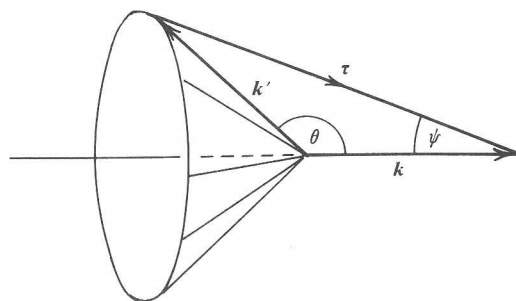
**Powder method.** A monochromatic beam of neutrons with wavevector  $k$  is incident on a powder sample, i.e. a sample of many small single crystals with random orientations. For a specified value of  $|\tau|$  ( $< 2k$ ), the wavevector  $k'$  of the scattered neutrons lies on a cone, known as a *Debye-Scherrer cone* (see Fig. 3.9). The axis of the cone is along  $k$  and its semi-angle  $\theta$  is given by (3.95). Only those microcrystals whose  $\tau$  vectors lie on a cone with axis along  $k$  and semi-angle

$$\psi = \frac{1}{2}\pi - \frac{1}{2}\theta \quad (3.102)$$

contribute to the scattering.

The direction of  $k$  is fixed. For each microcrystal, the vector  $\tau$  points in any direction in space with equal probability. Thus the

Fig. 3.9 Debye-Scherrer cone for Bragg scattering from a powder.



probability that the angle between  $\tau$  and  $k$  lies between  $\psi$  and  $\psi + d\psi$  is  $2\pi \sin \psi d\psi / 4\pi$ . Again we assume relaxed collimation. Then the total cross-section for each cone is

$$\begin{aligned} \sigma_{\text{tot } \tau}(\text{cone}) &= N \frac{(2\pi)^3}{v_0} \frac{2}{k} \sum_{\tau} |F_N(\tau)|^2 \int_0^{\pi/2} \delta(\tau^2 - 2k\tau \cos \psi)^{1/2} \sin \psi d\psi \\ &= \frac{V}{v_0^2} \frac{\lambda^3}{4 \sin \frac{1}{2}\theta} \sum_{\tau} |F_N(\tau)|^2. \end{aligned} \quad (3.103)$$

The sum over  $\tau$  is the sum over all reciprocal lattice vectors with the same value of  $|\tau|$ .

If the neutron detector is at a distance  $r$  from the target and has an effective diameter  $d$ , it intercepts a fraction  $d/2\pi r \sin \theta$  of the neutrons in the cone. The counting rate is therefore

$$P = \Phi \frac{d}{2\pi r \sin \theta} \sigma_{\text{tot } \tau}(\text{cone}), \quad (3.104)$$

where  $\Phi$  is the incident flux.

### 3.7 Coherent one-phonon scattering

#### Cross-sections

We return to the scattering from a Bravais crystal. The coherent one-phonon cross-section is obtained from (3.36) by taking the term  $\langle UV \rangle$  in the expansion of  $\exp\{\langle UV \rangle\}$ . From (3.23) and (3.24)

$$\langle \lambda | UV | \lambda \rangle = \sum_{ss'} \langle \lambda | (g_s a_s + g_s a_s^+) (h_{s'} a_{s'} + h_{s'}^* a_{s'}^+) | \lambda \rangle. \quad (3.105)$$

The matrix elements on the right-hand side are zero except for terms with  $a_s a_s^+$  and  $a_s^+ a_s$ . For these terms we have from (E.13)

$$\langle \lambda | a_s a_s^+ | \lambda \rangle = n_s + 1, \quad \langle \lambda | a_s^+ a_s | \lambda \rangle = n_s. \quad (3.106)$$

Thus  $\langle \lambda | UV | \lambda \rangle = \sum_s g_s h_s^* (n_s + 1) + g_s h_s n_s. \quad (3.107)$

From (3.25), (3.26) and (3.107) we have

$$\begin{aligned} \langle UV \rangle &= \sum_s g_s h_s^* \langle n_s + 1 \rangle + g_s h_s \langle n_s \rangle \\ &= \frac{\hbar}{2MN} \sum_s \frac{(\kappa \cdot e_s)^2}{\omega_s} [\exp\{-i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\} \langle n_s + 1 \rangle \\ &\quad + \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\} \langle n_s \rangle]. \end{aligned} \quad (3.108)$$



The expression for the coherent one-phonon cross-section is

$$\begin{aligned}
 & \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh 1 ph}} \\
 &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \exp(-2W) \sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}) \int_{-\infty}^{\infty} \langle UV \rangle \exp(-i\omega t) dt \\
 &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{1}{4\pi M} \exp(-2W) \sum_l \exp(i\mathbf{\kappa} \cdot \mathbf{l}) \sum_s \frac{(\mathbf{\kappa} \cdot \mathbf{e}_s)^2}{\omega_s} \\
 &\quad \times \int_{-\infty}^{\infty} [\exp\{-i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\} \langle n_s + 1 \rangle \\
 &\quad + \exp\{i(\mathbf{q} \cdot \mathbf{l} - \omega_s t)\} \langle n_s \rangle] \exp(-i\omega t) dt. \quad (3.109)
 \end{aligned}$$

The cross-section is the sum of two terms which arise from the two terms in the square brackets. Consider the first term. The integration with respect to  $t$  is

$$\int_{-\infty}^{\infty} \exp\{i(\omega_s - \omega)t\} dt = 2\pi\delta(\omega - \omega_s). \quad (3.110)$$

The summation with respect to  $l$  is

$$\sum_l \exp\{i(\mathbf{\kappa} - \mathbf{q}) \cdot \mathbf{l}\} = \frac{(2\pi)^3}{v_0} \sum_{\tau} \delta(\mathbf{\kappa} - \mathbf{q} - \boldsymbol{\tau}). \quad (3.111)$$

Thus the cross-section for the first term is

$$\begin{aligned}
 & \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh+1}} \\
 &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{(2\pi)^3}{v_0} \frac{1}{2M} \exp(-2W) \sum_s \sum_{\tau} \frac{(\mathbf{\kappa} \cdot \mathbf{e}_s)^2}{\omega_s} \langle n_s + 1 \rangle \\
 &\quad \times \delta(\omega - \omega_s) \delta(\mathbf{\kappa} - \mathbf{q} - \boldsymbol{\tau}). \quad (3.112)
 \end{aligned}$$

Similarly the cross-section for the second term is

$$\begin{aligned}
 & \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh-1}} \\
 &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{(2\pi)^3}{v_0} \frac{1}{2M} \exp(-2W) \sum_s \sum_{\tau} \frac{(\mathbf{\kappa} \cdot \mathbf{e}_s)^2}{\omega_s} \langle n_s \rangle \\
 &\quad \times \delta(\omega + \omega_s) \delta(\mathbf{\kappa} + \mathbf{q} - \boldsymbol{\tau}). \quad (3.113)
 \end{aligned}$$

The cross-section (3.112) contains the factors  $\delta(\omega - \omega_s)$  and  $\delta(\mathbf{\kappa} - \mathbf{q} - \boldsymbol{\tau})$ . So for scattering to occur two conditions must be satisfied:

$$\omega = \omega_s, \quad \mathbf{\kappa} = \boldsymbol{\tau} + \mathbf{q}. \quad (3.114)$$

From the definition of  $\omega$  (2.42), the first condition is

$$E - E' = \hbar\omega_s, \quad (3.115)$$

i.e. the energy of the neutron decreases by an amount equal to the energy of a phonon for the  $s$ th normal mode. So the scattering process is one in which the neutron creates a phonon. It is known as *phonon emission*. The energy for the phonon comes from the kinetic energy of the neutron. Eq. (3.115) can be written in the form

$$\frac{\hbar^2}{2m} (k^2 - k'^2) = \hbar\omega_s. \quad (3.116)$$

The second condition in (3.114) is

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} + \mathbf{q}, \quad (3.117)$$

$\mathbf{q}$  is the wavevector of the normal mode  $s$ . This equation may be regarded as an expression of conservation of momentum. If we multiply (3.117) by  $\hbar$ , the quantity  $\hbar(\mathbf{k} - \mathbf{k}')$  is the change in the momentum of the neutron, while  $\hbar(\boldsymbol{\tau} + \mathbf{q})$  is the momentum imparted to the crystal. However there is no physical significance to the separate terms  $\hbar\boldsymbol{\tau}$  and  $\hbar\mathbf{q}$ .

The cross-section (3.113) contains the term  $\delta(\omega + \omega_s)$  and  $\delta(\mathbf{\kappa} + \mathbf{q} - \boldsymbol{\tau})$ . The conditions that must be satisfied here are thus

$$\frac{\hbar^2}{2m} (k'^2 - k^2) = \hbar\omega_s, \quad (3.118)$$

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} - \mathbf{q}. \quad (3.119)$$

In this process the neutron annihilates a phonon in the  $s$ th normal mode. The energy of the phonon goes into an increase in the kinetic energy of the neutron. The process is known as *phonon absorption*.

Coherent one-phonon scattering may be regarded as elastic scattering in the frame of a crystal, whose atoms are displaced from their equilibrium positions with a sinusoidal variation given by the wavevector  $\mathbf{q}$ , and which is moving with the wave velocity of the phonon, i.e.  $\omega_s/q$ , in the direction of  $\mathbf{q}$ . The condition for constructive interference for waves scattered by a sinusoidally modulated lattice gives (3.117) and (3.119), while transforming the velocities of the incident and scattered neutrons in the crystal frame to their values in the laboratory frame gives the energy equations (3.116) and (3.118) – see Example 3.6. An optical analogue of the interference condition is provided by Fraunhofer diffraction from a grating which is ruled incorrectly, so that the spacing of the lines, instead of being constant,

has a sinusoidal variation. The main spectra are flanked by faint spectra known as *ghosts*. The wavevectors of the main spectra satisfy  $\kappa = \tau$ , while those of the ghosts satisfy  $\kappa = \tau \pm q$ .

We may note the factors  $\langle n_s + 1 \rangle$  and  $\langle n_s \rangle$  in the cross-sections (3.112) and (3.113). As  $T \rightarrow 0$ ,  $\langle n_s + 1 \rangle \rightarrow 1$  and  $\langle n_s \rangle \rightarrow 0$ . So the cross-section for phonon absorption tends to zero as the temperature tends to zero. This must be the case, because when the crystal is at zero temperature all the normal-mode oscillators are in their ground states. Thus there are no phonons to be absorbed.

It is straightforward to generalise the expressions in (3.112) and (3.113) to non-Bravais crystals. The cross-section for coherent one-phonon emission becomes

$$\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}+1} = \frac{k'}{k} \frac{(2\pi)^3}{2v_0} \sum_s \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} \exp(-W_d) \exp(i\kappa \cdot d)(\kappa \cdot e_{ds}) \right|^2 \times \langle n_s + 1 \rangle \delta(\omega - \omega_s) \delta(\kappa - q - \tau), \quad (3.120)$$

with a similar expression for the absorption cross-section. The notation is the same as on p. 37.

### Measurement of phonon dispersion relations

One of the most important applications of the coherent one-phonon scattering process is to measure the *phonon dispersion relations* for the crystal, that is, the frequency  $\omega_s$  as a function of wavevector  $q$  and polarisation index  $j$ . Before the advent of neutron scattering techniques these relations were largely unknown. Measurements of quantities like the specific heat give some average value of  $\omega_s$  for all the normal modes, but not the detailed function itself.

Suppose we do the following experiment. We allow a beam of monoenergetic neutrons to fall on a single crystal and measure the velocity distribution of the neutrons scattered in a fixed direction. The experiment is a straightforward one and can be done on a time-of-flight apparatus (see Brugger, 1965). Consider the measurements in reciprocal space (Fig. 3.10). The vector  $k$  ( $AO$  in the figure) is fixed relative to the reciprocal lattice of the crystal. Since the scattering angle is fixed, the vector  $k'$  lies along the line  $AD$ . The velocity of the scattered neutrons is proportional to  $k'$ . So analysing the scattered neutrons according to their velocity is equivalent to measuring the cross-section as a function of  $k'$ .

Consider the process of phonon absorption. To obtain coherent one-phonon scattering we must satisfy (3.118) and (3.119). Suppose we select an arbitrary value of  $k'$ , e.g.  $AB$  in Fig. 3.10. If (3.119) is to be satisfied that fixes  $q$  to be the vector  $TB$ . But in general none of the values of  $\omega_s$  for the normal modes with this wavevector satisfies (3.118). It is only for certain discrete values of  $k'$  ( $AC$  in the figure) that both conditions are satisfied, and coherent one-phonon scattering occurs.

Fig. 3.11 shows a graphical construction for obtaining these values of  $k'$  from the dispersion relations. Since  $k$  is fixed, the value of  $\omega_s$  required to satisfy (3.118) is a quadratic function of  $k'$  (curve 1 in the figure). If (3.119) is also to be satisfied, each value of  $k'$  fixes  $q$ , and we may therefore plot the dispersion relations as functions of  $k'$ . They are indicated schematically in the figure. Whenever curve 1 crosses one of the dispersion curves, both (3.118) and (3.119) are satisfied. Curve 2 represents  $\omega_s$  as a function of  $k'$  for (3.116), and when it crosses a dispersion curve the two conditions (3.116) and (3.117) for one-phonon emission are satisfied.

It is readily shown that whatever the form of the dispersion curves the two conditions for one-phonon absorption must be satisfied for at least one value of  $k'$  for each polarisation branch in every scattering direction. For  $k' = k$ , the value of  $\omega_s$  in curve 1 in Fig. 3.11 is zero, and hence less than the values on the dispersion curves at that  $k'$  value. As  $k'$  becomes large,  $\omega_s$  becomes large for curve 1 and eventually must be greater than the values on the dispersion curves, because the latter cannot exceed  $\omega_m$ , the maximum frequency of the normal modes in the crystal. Since all the curves are continuous, curve 1 must cross each of the three dispersion curves at least once. The same reasoning does not apply for one-phonon emission, and this process may not occur in some scattering directions.

If  $k$  and the crystal orientation are kept constant, the values of  $k'$  that satisfy the pair of conditions for one-phonon scattering define what is known as a *scattering surface*. There is one such surface for each polarisation branch. Sections through the scattering surfaces of aluminium for two values of  $k$  are shown in Fig. 3.12.

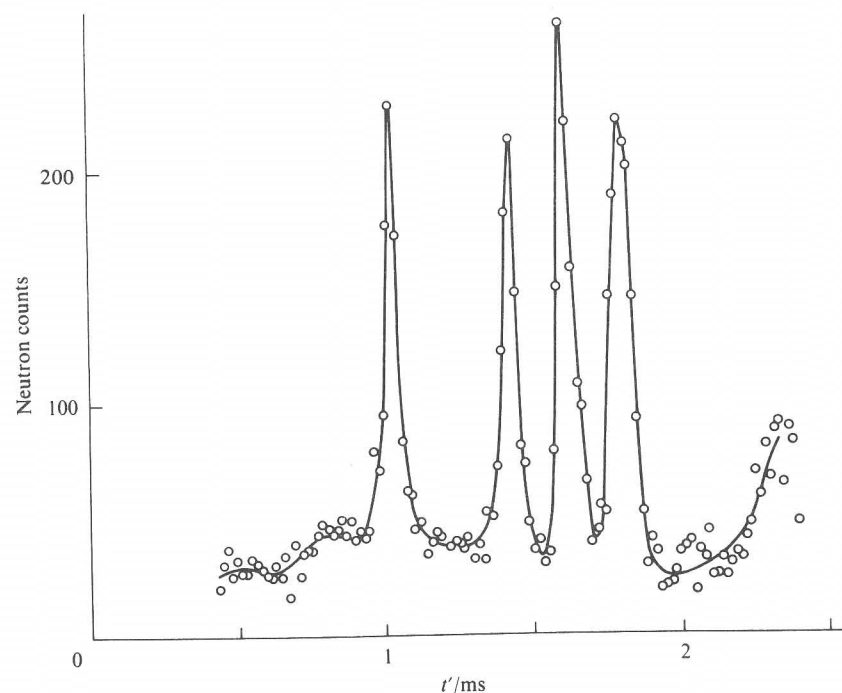
The curves in Fig. 3.12 are calculated from a set of theoretical dispersion relations for aluminium. But experimentally we proceed in the reverse direction. For fixed  $k$ , crystal orientation, and scattering direction, we measure a value of  $k'$  at which a coherent one-phonon peak occurs. We then substitute into (3.116)–(3.119), and hence



obtain  $\omega_s$  and  $q$  for a particular phonon. By varying the values of  $|k|$ , the angle between  $k$  and the crystal lattice, and the scattering angle, we may determine the  $\omega_s$  and  $q$  values for many phonons. Some results for magnesium, obtained with a time-of-flight spectrometer, are given in Figs. 3.13 and 3.14. Fig. 3.13 shows the time-of-flight spectrum of the scattered neutrons for fixed  $k$ ,  $\psi$ , and  $\theta$ . Fig. 3.14 shows the phonon frequencies obtained from a large number of such spectra.

The time-of-flight method of measuring phonon frequencies suffers from the disadvantage that we cannot preselect the  $q$  value of the phonon. However, a different technique, developed originally by Brockhouse (1960), overcomes this disadvantage. Crystals are used both to produce monoenergetic incident neutrons and to analyse the energy of the scattered neutrons. The apparatus is known as a *triple-*

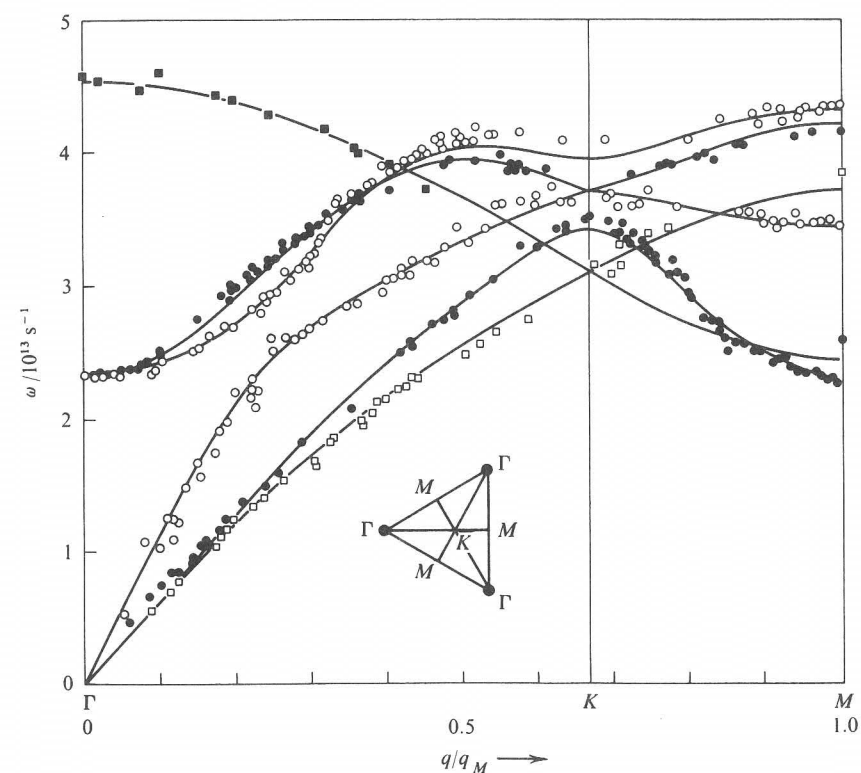
Fig. 3.13 Example of a time-of-flight spectrum for neutrons scattered in a fixed direction by a crystal of magnesium. The peaks are due to coherent one-phonon absorption. Part of the incoherent elastic peak can be seen on the right of the figure. (Squires, 1966.)



*axis spectrometer.* It is possible to control the experimental variables – the orientation of the various crystals, and the scattering angle – in such a way that the  $q$  value of the phonon to be measured is fixed at any required value. The method is particularly useful when we want to know how the frequency of a particular mode varies with, say, the temperature of the crystal. For a description of the triple-axis spectrometer, and its operation in the constant- $q$  mode, see Iyengar (1965) and Squires (1976).

By means of time-of-flight and crystal spectrometers the phonon dispersion relations have been determined for a large number of crystalline materials, including metallic, ionic, covalent, and rare-gas

Fig. 3.14 Phonon frequencies of magnesium at 290 K along the direction  $\Gamma KM$ . The curves correspond to an eight-neighbour axial-force model. Inset: symmetry plane in reciprocal space perpendicular to the hexad axis showing the direction  $\Gamma KM$ . (Pynn and Squires, 1972.)



crystals. The object of the measurements is to obtain information about the interatomic forces. A variety of methods have been proposed for interpreting the results. Some employ empirical models with force constants treated as adjustable parameters; others are based on more physical models. A systematic survey of the experimental results, together with a review of the theories, will be found in Venkataraman, Feldkamp, and Sahni (1975). For a briefer account see Cochran (1973).

### Polarisation vectors

We may note the term  $(\kappa \cdot e_s)^2$  in the cross-sections (3.112) and (3.113). From measurements of the intensities of the peaks for one-phonon scattering, it is possible, in principle, to deduce the polarisation vectors  $e_s$ . There have not been many systematic measurements of this kind, but Brockhouse *et al.* (1963) have reported some on sodium and germanium.

In general the vectors  $e_s$  corresponding to a given wavevector  $q$  are not related in a simple way to the direction of  $q$ . But in certain cases there is a simple relation. For example, if  $q$  lies in the (001) plane of a cubic crystal, one of the  $e_s$  is along the [001] axis. If the scattering geometry is arranged so that  $\kappa$  is in the (001) plane,  $(\kappa \cdot e_s)$  is zero for this mode. The result is sometimes used in one-phonon measurements to eliminate the effects of one of the polarisation branches.

### Anharmonic forces

Although ideally the velocity spectrum of neutrons scattered in coherent one-phonon processes is a set of  $\delta$ -functions, in practice the peaks have finite widths. The broadening arises from several factors. The first is the resolution of the apparatus. The wavevectors  $k$  and  $k'$  have a finite spread in magnitude and direction. Secondly the crystal has a mosaic spread. The third and most interesting reason is that the interatomic forces in the crystal are not truly harmonic.

The analysis of the displacements of the atoms from their equilibrium positions in terms of a set of non-interacting normal modes is only correct for pure harmonic forces. In fact the forces have an anharmonic component (otherwise the crystal would not expand on heating) which causes the normal modes to interact with each other. The energy in a mode does not remain constant, but is gradually

transferred to other modes. Thus the mode is represented in time by a damped sinusoidal wave, which means that its frequency is no longer sharp. It is spread over a finite range; the greater the anharmonic component, the greater the spread. Hence the scattered neutron groups occur, not at a sharp value of  $k'$ , but over a range of values.

As the temperature of the crystal is raised, the anharmonic component of the forces increases, and the widths of the neutron peaks increase. By measuring the widths we can study the anharmonic contribution to the forces. In addition to broadening the frequencies of the normal modes, anharmonic forces also produce changes in the mean values of the frequencies. Both effects have been measured. A discussion of the theory of anharmonic forces in crystals, together with references to experimental work, will be found in Cowley (1968).

### 3.8 Coherent multiphonon scattering

The coherent two-phonon cross-section is obtained from (3.36) by taking the term  $(1/2!)(UV)^2$  in the expansion of  $\exp(UV)$ . It can readily be shown that the cross-section contains two  $\delta$ -function terms which give rise to the equations

$$\frac{\hbar^2}{2m}(k^2 - k'^2) = \hbar(\pm\omega_{s_1} \pm \omega_{s_2}), \quad (3.121)$$

$$k - k' = \tau \pm q_1 \pm q_2. \quad (3.122)$$

Both conditions must be satisfied. The neutron is scattered having simultaneously created or annihilated a single phonon in two different normal modes.

In the one-phonon process we saw that for fixed  $k$ , scattering angle, and crystal orientation, scattering occurs only for discrete values of  $k'$ . However, in the two-phonon process, if we select an arbitrary  $k'$  within a certain range, we can always find combinations of two normal modes whose  $q$  and  $\omega_s$  values satisfy (3.121) and (3.122). So two-phonon scattering does not give rise to peaks in the velocity spectrum of the scattered neutrons. It gives a continuous spectrum; in other words it adds to the background (Fig. 3.13). This is fortunate, as it enables us to separate the effects of one- and two-phonon scattering.

For higher phonon processes, we get two equations like (3.121) and (3.122) with additional terms  $-\omega_{s_3}$ ,  $q_3$  and so on. It is true, a



*fortiori*, that for an arbitrary value of  $k'$  we can find combinations of normal modes to satisfy the two equations.

### 3.9 Incoherent scattering

The basic expression for the incoherent scattering cross-section is given in (2.69). We consider a Bravais crystal and put

$$\mathbf{R}_l(t) = \mathbf{l} + \mathbf{u}_l(t). \quad (3.123)$$

Then

$$\begin{aligned} & \sum_l \int \langle \exp\{-i\mathbf{k} \cdot \mathbf{R}_l(0)\} \exp\{i\mathbf{k} \cdot \mathbf{R}_l(t)\} \rangle \exp(-i\omega t) dt \\ &= N \int \langle \exp\{-i\mathbf{k} \cdot \mathbf{u}_0(0)\} \exp\{i\mathbf{k} \cdot \mathbf{u}_0(t)\} \rangle \exp(-i\omega t) dt \\ &= N \int \langle \exp U \exp V_0 \rangle \exp(-i\omega t) dt, \end{aligned} \quad (3.124)$$

$$\text{where } U = -i\mathbf{k} \cdot \mathbf{u}_0(0), \text{ and } V_0 = i\mathbf{k} \cdot \mathbf{u}_0(t). \quad (3.125)$$

In summing over  $l$  in (3.124) we have used the result that for a Bravais crystal all the terms in the sum are equal.  $U$  is the same as the previous  $U$ , defined in (3.23).  $V_0$  is the previous  $V$  (3.24) evaluated at  $l = 0$ . From (3.35)

$$\langle \exp U \exp V_0 \rangle = \exp\langle U^2 \rangle \exp\langle UV_0 \rangle. \quad (3.126)$$

Thus

$$\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \exp\langle U^2 \rangle \int \exp\langle UV_0 \rangle \exp(-i\omega t) dt. \quad (3.127)$$

As before  $\exp\langle UV_0 \rangle$  is expanded in powers of  $\langle UV_0 \rangle$ . The  $p$ th term corresponds to a  $p$ -phonon process.

To calculate the incoherent elastic scattering we replace  $\exp\langle UV_0 \rangle$  by unity in (3.127) and use the results (3.42) and (3.43). We then integrate with respect to  $E'$ , and obtain the result

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{inc el}} = \frac{\sigma_{\text{inc}}}{4\pi} N \exp(-2W). \quad (3.128)$$

The only dependence of this cross-section on the scattering direction is in the Debye-Waller factor, which depends on  $\mathbf{k}$ . At low temperatures the Debye-Waller factor is close to unity, and the scattering is almost isotropic.

The incoherent one-phonon cross-section is obtained from (3.127) by replacing  $\exp\langle UV_0 \rangle$  by  $\langle UV_0 \rangle$ . From (3.108)

$$\langle UV_0 \rangle = \frac{\hbar}{2MN} \sum_s (\mathbf{k} \cdot \mathbf{e}_s)^2 \frac{1}{\omega_s} \{ \langle n_s + 1 \rangle \exp(i\omega_s t) + \langle n_s \rangle \exp(-i\omega_s t) \}, \quad (3.129)$$

$$\begin{aligned} \left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc 1 ph}} &= \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{1}{2M} \exp(-2W) \sum_s \frac{(\mathbf{k} \cdot \mathbf{e}_s)^2}{\omega_s} \\ &\quad \times \{ \langle n_s + 1 \rangle \delta(\omega - \omega_s) + \langle n_s \rangle \delta(\omega + \omega_s) \}. \end{aligned} \quad (3.130)$$

The first term in the curly brackets corresponds to phonon emission and the second to phonon absorption.

Consider the emission cross-section. It contains only one  $\delta$ -function,  $\delta(\omega - \omega_s)$ . Thus only the energy condition

$$\omega = \omega_s \quad \text{or} \quad \frac{\hbar^2}{2m} (k^2 - k'^2) = \hbar\omega_s \quad (3.131)$$

needs to be satisfied. For incoherent scattering there is no interference condition like (3.117). Therefore, for a given  $\mathbf{k}$ ,  $\theta$ , and crystal orientation, incoherent one-phonon scattering occurs for a continuous range of  $k'$  values. For a given  $k'$ , we get scattering from all normal modes whose  $\omega_s$  values satisfy (3.131). The cross-section therefore depends on the number of modes that have the correct frequency. We can express the cross-section in terms of the phonon density of states  $Z(\omega)$ .

$$\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc+1}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{3N}{2M} \exp(-2W) \frac{\langle (\mathbf{k} \cdot \mathbf{e}_s)^2 \rangle_{\text{av}}}{\omega} Z(\omega) \langle n + 1 \rangle, \quad (3.132)$$

$$\text{where } \omega = (E - E')/\hbar, \quad (3.133)$$

$$\text{and } \langle n + 1 \rangle = \frac{1}{2} \{ \coth(\frac{1}{2}\hbar\omega\beta) + 1 \}. \quad (3.134)$$

The quantity  $\langle (\mathbf{k} \cdot \mathbf{e}_s)^2 \rangle_{\text{av}}$  is the value of  $(\mathbf{k} \cdot \mathbf{e}_s)^2$  averaged over all the modes with frequency  $\omega$ . For a cubic crystal

$$\langle (\mathbf{k} \cdot \mathbf{e}_s)^2 \rangle_{\text{av}} = \frac{1}{3} k^2, \quad (3.135)$$

and the incoherent one-phonon cross-sections are given by

$$\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}\pm 1} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{N}{4M} k^2 \exp(-2W) \frac{Z(\omega)}{\omega} \{ \coth(\frac{1}{2}\hbar\omega\beta) \pm 1 \}. \quad (3.136)$$

By measuring the incoherent one-phonon scattering as a function of  $E'$  for a cubic crystal, the phonon density of states may be



determined. The method has been used for vanadium where the scattering is almost entirely incoherent ( $\sigma_{\text{coh}} = 0.02 \times 10^{-28} \text{ m}^2$ ,  $\sigma_{\text{inc}} = 5.0 \times 10^{-28} \text{ m}^2$ ). Some results are shown in Fig. 3.15. A basic difficulty of the method is that incoherent scattering from multiphonon processes also occurs. Both one-phonon and multiphonon processes give incoherent scattering over a continuous range of  $k'$  values, and it is not easy to estimate the contribution of the latter.

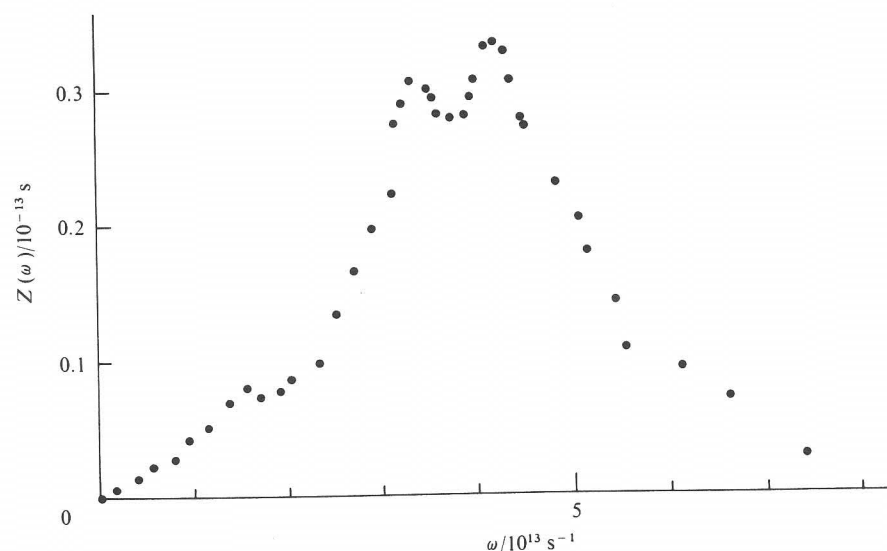
To obtain the incoherent cross-sections for non-Bravais crystals we proceed as in Section 3.6. The elastic cross-section is

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{inel}} = N \sum_d \{\bar{b}_d^2 - (\bar{b}_d)^2\} \exp(-2W_d). \quad (3.137)$$

The incoherent one-phonon emission cross-section is

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}+1} &= \frac{k'}{k} \sum_d \frac{1}{2M_d} \{\bar{b}_d^2 - (\bar{b}_d)^2\} \exp(-2W_d) \\ &\times \sum_s \frac{|\kappa \cdot e_{ds}|^2}{\omega_s} \langle n_s + 1 \rangle \delta(\omega - \omega_s). \end{aligned} \quad (3.138)$$

Fig. 3.15 Phonon density of states of vanadium from measurements of incoherent scattering. (After Gläser *et al.*, 1965.)



### 3.10 Multiphonon cross-sections – approximation methods

We have seen that the measurement of one-phonon cross-sections provides useful information. From coherent one-phonon scattering we may obtain dispersion relations. From incoherent one-phonon scattering we may determine the phonon density of states – at any rate for a cubic crystal. Multiphonon processes do not in general give useful information. They just add to the background scattering. Nevertheless we sometimes need to estimate their cross-sections, if only to subtract their contribution to the total scattering. There are two basic difficulties. The first is that as the energy  $E$  of the incident neutron increases and as the temperature  $T$  of the crystal increases, the convergence of the phonon expansion becomes progressively worse. The second is that, as the number of phonons in the scattering process increases, the cross-section – especially the coherent one – becomes more and more laborious to calculate. Several approximation methods have been devised to overcome these difficulties. We shall mention two.

#### Incoherent approximation

We write the cross-sections for a process in which  $p$  phonons are exchanged between the neutron and the crystal in the form

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh } p} = \sigma_{\text{coh}} F_{\text{coh } p}, \quad (3.139)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc } p} = \sigma_{\text{inc}} F_{\text{inc } p}. \quad (3.140)$$

Then the incoherent approximation is to assume that for  $p \geq 2$

$$F_{\text{coh } p} = F_{\text{inc } p}. \quad (3.141)$$

$F_{\text{coh } p}$  is made up of terms from atoms  $l$  and  $l'$  with both  $l = l'$  and  $l \neq l'$ , while  $F_{\text{inc } p}$  is made up only of terms  $l = l'$ . The justification for the incoherent approximation is that for processes involving two or more phonons the cross-sections for both coherent and incoherent scattering are smoothly varying functions of the scattered energy, the incident energy, and the scattering angle. It therefore appears that the interference terms  $l \neq l'$  in the coherent cross-section cancel each other to a large extent.

The usefulness of the approximation is that it is much easier to calculate  $F_{\text{inc } p}$  than  $F_{\text{coh } p}$ . So to calculate  $(d^2\sigma/d\Omega dE')_{\text{coh } p}$  we

calculate  $F_{\text{inc } p}$  and multiply by  $\sigma_{\text{coh}}$ . For a discussion of the validity of the approximation see Placzek and Van Hové (1955).

### Mass expansion

The mass expansion is a method of calculating the total cross-section – defined in (1.13) – for incoherent scattering by a powder sample or polycrystal. This cross-section is the sum of the elastic and inelastic terms. We have seen that the phonon expansion corresponds to expanding the term  $\exp(UV_0)$  in the expression for the cross-section in (3.127). Placzek (1954) pointed out that provided  $M$ , the mass of a nucleus in the crystal, is large compared to  $m$ , the mass of the neutron, a more rapidly converging series is obtained by taking the Debye–Waller factor  $\exp\langle U^2 \rangle$  together with  $\exp(UV_0)$  and expanding  $\exp \gamma$ , where  $\gamma = \langle U^2 \rangle + \langle UV_0 \rangle$ . This is the *mass expansion*, so called because  $\gamma$  is proportional to  $m/M$ . As the neutron energy  $E$  and the crystal temperature  $T$  rise, the total elastic cross-section falls, because  $\langle U^2 \rangle$  (which is a negative quantity) becomes numerically large, and the Debye–Waller factor becomes small. On the other hand, the inelastic cross-section rises, because  $\langle UV_0 \rangle$  (a positive quantity) also becomes large.† However the quantity  $\gamma$  remains relatively small.

The evaluation of the terms in the mass expansion is usually made on the basis of the Debye approximation, i.e. all the normal modes are assumed to have the same velocity, irrespective of wavevector and polarisation. The cross-section, in units of  $\sigma_{\text{inc}}$ , is then a function of the three parameters  $m/M$ ,  $x = (E/k_B\theta_D)^{1/2}$ , and  $\theta = T/\theta_D$ , where  $\theta_D$  is the Debye temperature of the crystal. Algebraic expressions for the first few terms are given in Placzek (1957), and a table of numerical values for a range of  $x$  and  $\theta$  is given in Marshall and Lovesey (1971).

The mass expansion may be used in conjunction with the incoherent approximation to obtain an estimate of the total coherent cross-section. However, care is needed at low incident energies, when the incoherent approximation is a poor one for elastic scattering. The total incoherent elastic cross-section is a smoothly varying function of the neutron energy, whereas its coherent counterpart shows dis-

† It may be noted that as  $E$  tends to zero the elastic cross-section tends to a constant, but the inelastic cross-section does not tend to zero. As  $E$  becomes small compared to  $\hbar\omega_m$  the inelastic cross-section starts to rise, being proportional to  $1/k$ .

continuities as the various crystal planes start to contribute to the scattering. In that case the total incoherent elastic cross-section, calculated from (3.128), is subtracted from the mass expansion estimate to give the inelastic term. The incoherent approximation is then applied to the latter. The total coherent elastic cross-section is obtained separately by summing the expression in (3.103) over all  $\tau$  (other than zero) for which  $\tau < 2k$ .

### Examples

3.1 (a) Derive the dispersion relation (G.4) for a one-dimensional crystal of identical atoms with harmonic forces.

(b) Derive the expressions (G.12) and (G.13) for the kinetic and potential energies of the crystal.

(c) Show that the time-averaged values of the kinetic and potential energies are equal.

3.2 Show that as the temperature becomes large ( $k_B T \gg \hbar\omega$ ) the expression given in (3.19) and (3.20) for the probability function of a harmonic oscillator tends to the classical expression.

3.3 Show that, for a cubic Bravais crystal, the Debye–Waller factor  $\exp(-2W)$  depends on  $1/\omega$  for  $k_B T \ll \hbar\omega_m$ , and  $1/\omega^2$  for  $k_B T \gg \hbar\omega_m$ , where the average is taken over all normal modes.

3.4 Prove that, for a cubic Bravais crystal having a Debye frequency spectrum with Debye temperature  $\theta_D$ , the mean square displacement of an atom is given by

$$\langle u^2 \rangle = \frac{9}{4} \frac{\hbar^2}{M} \frac{1}{k_B \theta_D}, \quad T \ll \theta_D,$$

$$\langle u^2 \rangle = 9 \frac{\hbar^2}{M} \frac{T}{k_B \theta_D^2}, \quad T \gg \theta_D.$$

3.5 (a) Estimate the rms displacement of an atom in copper at  $T = 20$  K, and at  $T = 1000$  K.

(b) Neutrons are Bragg scattered by the (111) plane in a copper crystal. By what factor does the intensity of the peak diminish when the temperature of the crystal is changed from 20 K to 1000 K? (Assume a Debye spectrum with  $\theta_D = 320$  K. Copper has an atomic weight of 64 and a face-centred cubic structure with cube side =  $3.61 \text{ \AA}$ .)

3.6 Coherent one-phonon scattering may be regarded as elastic scattering in the rest-frame of a moving crystal whose atoms are displaced with a sinusoidal variation. Show that, if the position of atom  $l$  in a Bravais crystal is given by

$$\mathbf{R}_l = \mathbf{l} + \mathbf{A} \cos(\mathbf{q} \cdot \mathbf{l}), \quad \text{where } \mathbf{A} \cdot \boldsymbol{\kappa} \ll 1,$$

and the velocity of the crystal is  $\omega_s/q$  in the direction of  $\mathbf{q}$ , this picture leads to the relations

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} \pm \mathbf{q}, \quad \frac{\hbar^2}{2m} (k^2 - k'^2) = \pm \hbar \omega_s.$$

3.7 The point  $\boldsymbol{\tau} = 0$  is always a point on the coherent one-phonon scattering surface. (It corresponds to the undisturbed incident beam.) Show that whether it is an isolated point, or whether the scattering surface for a given polarisation branch exists in the neighbourhood of  $\boldsymbol{\tau} = 0$ , depends on whether the velocity of the incident neutrons is less or greater than the velocity of sound for the branch. (Assume for simplicity that the velocity of sound  $c$  is independent of the direction of propagation.)

3.8 Show from the form of the coherent one-phonon absorption cross-section that for fixed  $\mathbf{k}'$  this cross-section is proportional to  $1/k$  (i.e. to  $1/v$ ) as  $k$  tends to zero. Interpret this result physically.

## 4

### Correlation functions in nuclear scattering

In the present chapter we relate the cross-sections for neutron scattering to thermal averages of operators belonging to the scattering system. The thermal averages can be expressed in terms of what are known as *correlation functions*. These functions are not only useful for calculating various properties of the scattering system, but they also provide insight into the physical significance of the terms that occur in the scattering cross-sections. This formulation of the subject is due primarily to Van Hove (1954). The calculations are quite general and refer to any system, solid, liquid, or gas, for which the scattering can be divided into coherent and incoherent parts.

#### 4.1 Definitions of $I(\boldsymbol{\kappa}, t)$ , $G(\mathbf{r}, t)$ , and $S(\boldsymbol{\kappa}, \omega)$

We start with the expression (2.68) for the coherent scattering cross-section before we particularised it to a crystal target.

$$\left( \frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \int \sum_{jj'} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} \rangle \times \exp(-i\omega t) dt. \quad (4.1)$$

We define a function  $I(\boldsymbol{\kappa}, t)$ , known as the *intermediate function*, by

$$I(\boldsymbol{\kappa}, t) = \frac{1}{N} \sum_{jj'} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} \rangle, \quad (4.2)$$

where  $N$  is the number of nuclei in the scattering system.

We next define functions  $G(\mathbf{r}, t)$  and  $S(\boldsymbol{\kappa}, \omega)$  by

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I(\boldsymbol{\kappa}, t) \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}) d\boldsymbol{\kappa}, \quad (4.3)$$