

where c_ξ is the relative abundance of the ξ th isotope, I_ξ its nuclear spin, and b_ξ^+ and b_ξ^- 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 σ_{coh} and σ_{inc} defined in (2.70). A list of the values of σ_{coh} and σ_{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 σ_{coh} and σ_{inc}

Element or nuclide	Z	σ_{coh}	σ_{inc}	Element	Z	σ_{coh}	σ_{inc}
^1H	1	1.8	80.2	V	23	0.02	5.0
^2H	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 σ_{coh} and σ_{inc} are 10^{-28} 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.

3

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

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

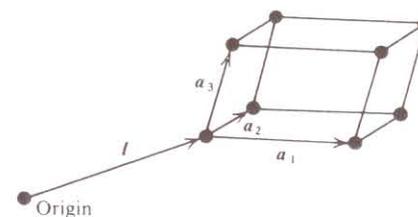
We define the reciprocal lattice to be a lattice with unit-cell vectors $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, $\boldsymbol{\tau}_3$, where

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

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.



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

Owing to thermal motion the nucleus l is displaced from its equilibrium position l . Its instantaneous position is

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

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

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

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

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

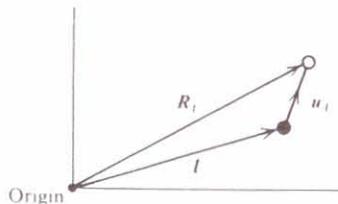
$$\mathbf{R}_l(t) = l + \mathbf{u}_l(t), \quad (3.9)$$

which follows from (3.6), since 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 displacements

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



ments due to a set of normal modes. Thus

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

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 . ω_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^+ , 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^+ by their Heisenberg operators, $a_s(t)$ and $a_s^+(t)$. It is shown in Appendix E.1 that

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

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

Thus

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

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 ψ_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 ψ_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

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

where

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

M is the mass of the particle, and ω 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)

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

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 $U + V$.

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

From (3.31) and (3.32)

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

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 κ 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

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

3.5 Phonon expansion

A crystal of N atoms has $3N$ normal modes. The initial state λ 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 λ' , 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 α , 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 α and β , 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 α is in turn each of the numbers 1 to $3N$, and, for each α , n_α 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 α, β is in turn each of the $3N(3N-1)/2$ combinations of two oscillators selected from $3N$, and, for each combination, n_α and n_β 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 λ' , sum only over those λ' which, for a fixed λ , correspond to a p -phonon process. Then average over λ 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 δ -functions which show that the process is elastic, one-phonon, two-phonon, and so on. This is the line we shall follow.

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 λ 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 τ_1 and τ_2 , and θ_1 and θ_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 τ , the value of k must be greater than $\frac{1}{2}\tau$, otherwise (3.95) cannot be satisfied.

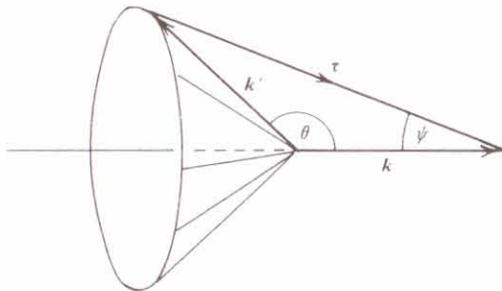
Powder method. A monochromatic beam of neutrons with wavevector k is incident on a powder sample, i.e. a sample of many small single crystals with random orientations. For a specified value of $|\tau|$ ($< 2k$), the wavevector k' of the scattered neutrons lies on a cone, known as a *Debye-Scherrer cone*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

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

The sum over τ 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 Φ 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 $\langle \lambda | UV | \lambda \rangle = \sum_s g_s h_s^* (n_s + 1) + g_s h_s n_s$. (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

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

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

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

Thus the cross-section for the first term is

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

Similarly the cross-section for the second term is

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

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 ω (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. ω_s/\mathbf{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

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

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 ω_s as a function of wavevector \mathbf{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 ω_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 \mathbf{k} (AO in the figure) is fixed relative to the reciprocal lattice of the crystal. Since the scattering angle is fixed, the vector \mathbf{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 \mathbf{q} to be the vector TB . But in general none of the values of ω_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 ω_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 \mathbf{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 ω_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 ω_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, ω_s becomes large for curve 1 and eventually must be greater than the values on the dispersion curves, because the latter cannot exceed ω_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

Fig. 3.10 Diagram in reciprocal space for coherent one-phonon scattering;
 ● reciprocal lattice point.

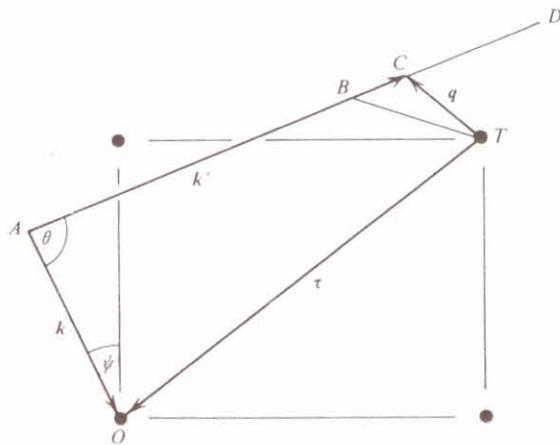


Fig. 3.11 Coherent one-phonon scattering: diagram for determining values of k' for fixed k , ψ , and θ .

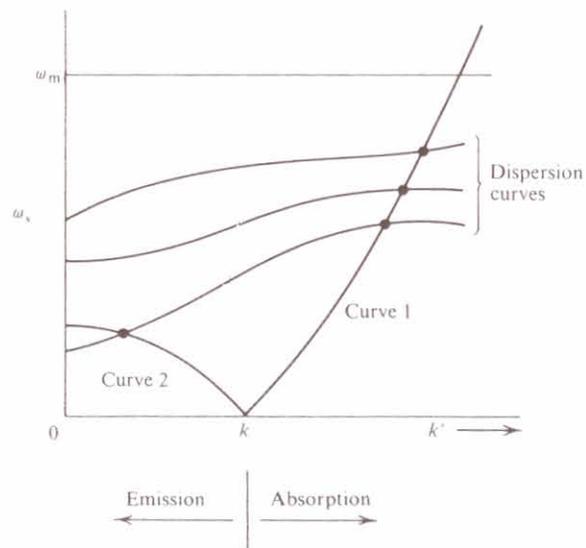
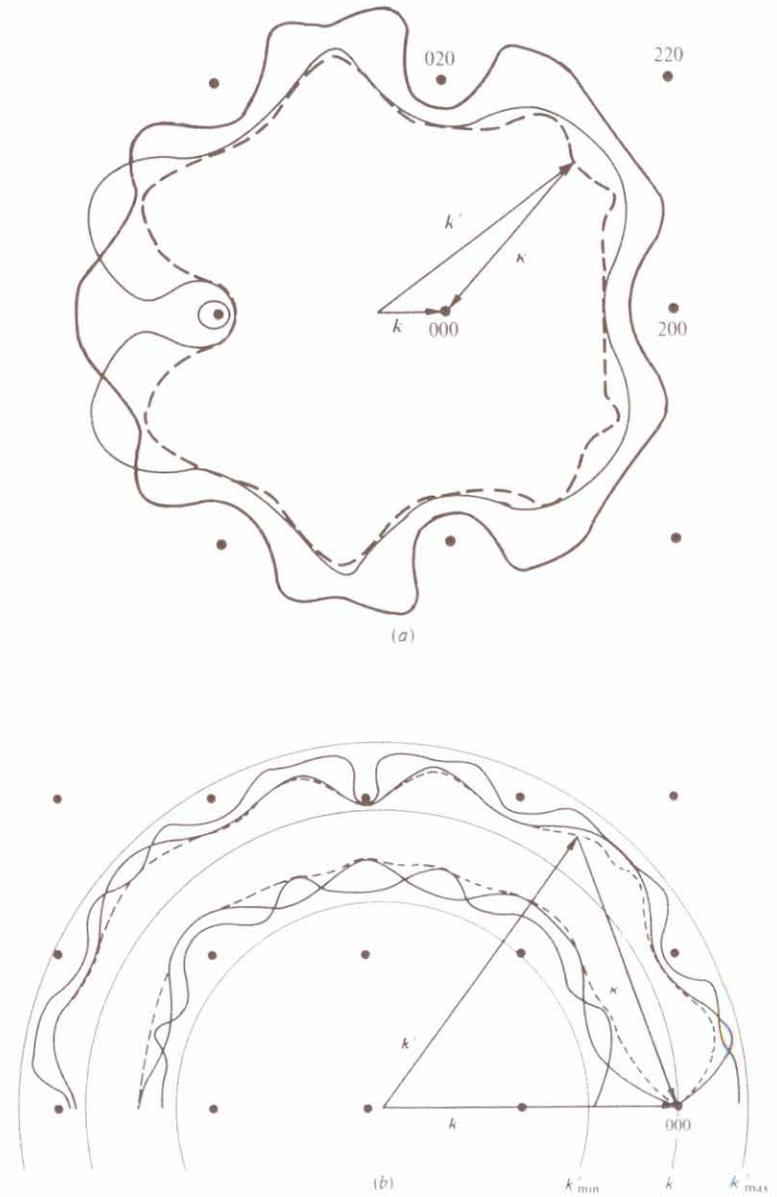


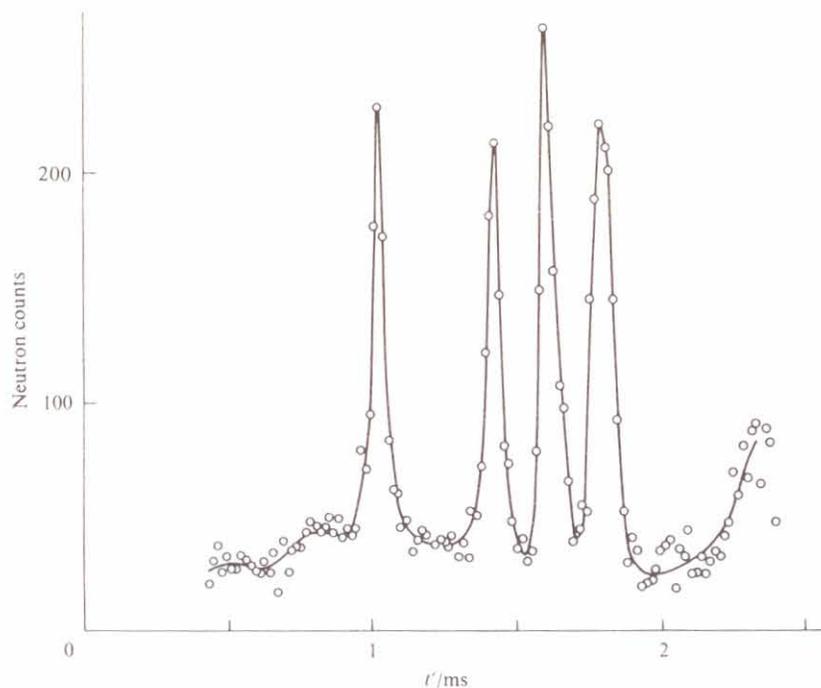
Fig. 3.12 Sections through the scattering surfaces of aluminium in the (001) plane (a) for incident neutrons of wavelength 6.74 Å, and (b) for incident neutrons of wavelength 1.08 Å. (Squires, 1956.)



obtain ω , and q for a particular phonon. By varying the values of $|\mathbf{k}|$, the angle between \mathbf{k} and the crystal lattice, and the scattering angle, we may determine the ω , 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 \mathbf{k} , ψ , and θ . 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-*

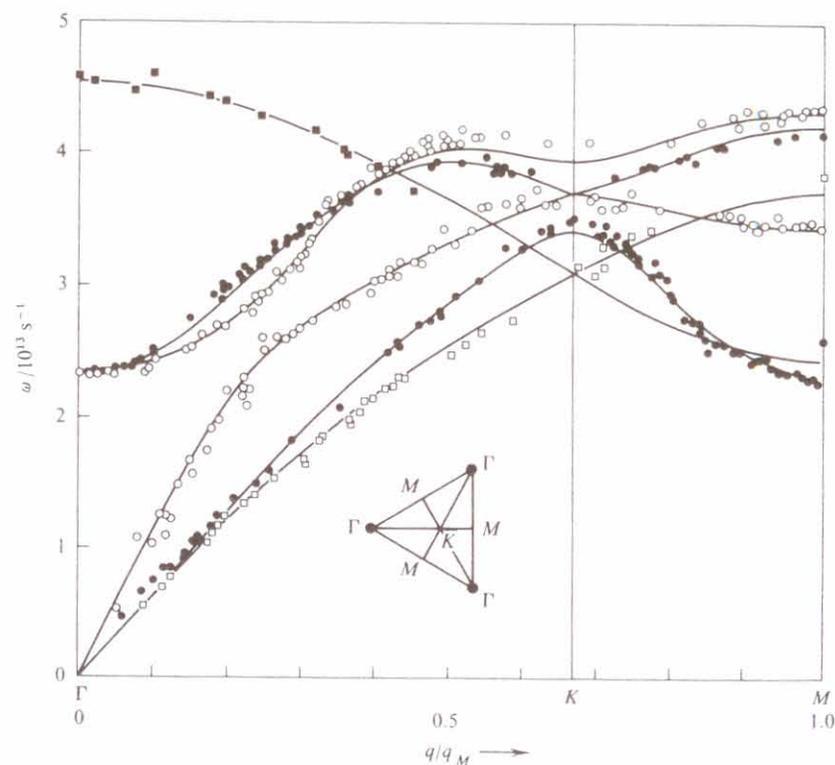
Fig. 3.13 Example of a time-of-flight spectrum for neutrons scattered in a fixed direction by a crystal of magnesium. The peaks are due to coherent one-phonon absorption. Part of the incoherent elastic peak can be seen on the right of the figure. (Squires, 1966.)



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 ΓKM . The curves correspond to an eight-neighbour axial-force model. Inset: symmetry plane in reciprocal space perpendicular to the hexad axis showing the direction ΓKM . (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 $(\boldsymbol{\kappa} \cdot \mathbf{e}_s)^2$ 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 \mathbf{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 \mathbf{e}_s corresponding to a given wavevector \mathbf{q} are not related in a simple way to the direction of \mathbf{q} . But in certain cases there is a simple relation. For example, if \mathbf{q} lies in the (001) plane of a cubic crystal, one of the \mathbf{e}_s is along the [001] axis. If the scattering geometry is arranged so that $\boldsymbol{\kappa}$ is in the (001) plane, $(\boldsymbol{\kappa} \cdot \mathbf{e}_s)$ 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 δ -functions, in practice the peaks have finite widths. The broadening arises from several factors. The first is the resolution of the apparatus. The wavevectors \mathbf{k} and \mathbf{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 \mathbf{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 δ -function terms which give rise to the equations

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

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} \pm \mathbf{q}_1 \pm \mathbf{q}_2. \quad (3.122)$$

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 \mathbf{k} , scattering angle, and crystal orientation, scattering occurs only for discrete values of \mathbf{k}' . However, in the two-phonon process, if we select an arbitrary \mathbf{k}' within a certain range, we can always find combinations of two normal modes whose \mathbf{q} and ω_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 $-\omega_{s_3}$, \mathbf{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

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

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

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

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

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 $\boldsymbol{\kappa}$. 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)

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

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

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 δ -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} , θ , 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 ω_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 $Z(\omega)$.

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

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

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

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

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

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

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

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