4.1. THERMAL DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

$$\frac{d\sigma}{d\Omega} = \langle |Y(Q)|^2 \rangle,$$

where

$$Y(Q) = \sum_{\kappa l} f_\kappa(\mathbf{Q}) \exp\{i\mathbf{Q} \cdot [\mathbf{r}(\kappa l) + \mathbf{u}(\kappa l)]\}. \qquad (4.1.3.1)$$

The angled brackets indicate an average value over a period of time much longer than the period of oscillation of an atom. **Q** is the 'scattering vector' defined by

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}_0,$$

where **k** and $\mathbf{k}_0$ are the wavevectors (each of magnitude $2\pi/\lambda$) of the scattered and incident beams, respectively. The magnitude of **Q** is $4\pi(\sin\theta)/\lambda$, where 2θ is the angle between **k** and $\mathbf{k}_0$. $f_\kappa(\mathbf{Q})$ is the scattering factor of the κth atom in the unit cell.

The cross section $d\sigma/d\Omega$ can be expanded as a power series:

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)^{(0)} + \left(\frac{d\sigma}{d\Omega}\right)^{(1)} + \left(\frac{d\sigma}{d\Omega}\right)^{(2)} + \ldots . \qquad (4.1.3.2)$$

The individual terms on the right-hand side refer to the cross sections for zero-order, first-order, second-order scattering . . ., *i.e.* for processes involving no exchange of energy between the incident radiation and the crystal (Bragg scattering), the exchange of one quantum of lattice vibrational energy (one-phonon scattering), the exchange of two quanta (two-phonon scattering) . . ..

The instantaneous thermal displacement $\mathbf{u}(\kappa l)$ of the atom (κl) can be expressed, using equations (4.1.2.3), (4.1.2.6), (4.1.2.7) and (4.1.2.8), as a superposition of the displacements of the $3nN$ ($\sim 10^{23}$) independent normal modes of vibration:

$$\mathbf{u}(\kappa l) = [Nm(\kappa)]^{-1/2} \sum_{j\mathbf{q}} \frac{E_j^{-1/2}(\mathbf{q})}{\omega_j^2(\mathbf{q})} \mathbf{e}(\kappa|j\mathbf{q})$$
$$\times \exp\{i[\mathbf{q}\cdot\mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}. \qquad (4.1.3.3)$$

Explicit expressions can now be given for the partial cross sections in equation (4.1.3.2). The cross section for Bragg scattering is

$$\left(\frac{d\sigma}{d\Omega}\right)^{(0)} = N|F(\mathbf{Q})|^2 \frac{(2\pi)^3}{\mathbf{v}} \sum_{\mathbf{h}} \delta(\mathbf{Q} - \mathbf{Q_h}), \qquad (4.1.3.4)$$

where **v** is the cell volume. The delta function requires that

$$\mathbf{Q} = \mathbf{Q_h},$$

where $\mathbf{Q_h}$ is a reciprocal-lattice vector, so that scattering is restricted to the points **h** of the reciprocal lattice. The structure factor $F(\mathbf{Q})$ is

$$F(\mathbf{Q}) = \sum_\kappa f_\kappa(\mathbf{Q}) \exp[i\mathbf{Q}\cdot\mathbf{r}(\kappa)] \exp(-W_\kappa),$$

where the exponent W_κ of the temperature factor of the atom κ is calculated by summing over the normal modes:

$$W_\kappa = \frac{1}{2Nm(\kappa)} \sum_{j\mathbf{q}} |\mathbf{Q}_h \cdot \mathbf{e}(\kappa|j\mathbf{q})|^2 \frac{E_j(\mathbf{q})}{\omega_j^2(\mathbf{q})}. \qquad (4.1.3.5)$$

The last equation shows that the acoustic modes, with frequencies approaching zero as $\mathbf{q} \to 0$, make the largest contribution to the temperature factor.

The one-phonon cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)^{(1)} = \frac{(2\pi)^3}{\mathbf{v}} \sum_{j\mathbf{q}} \frac{|G_j(\mathbf{Q},\mathbf{q})|^2 E_j(\mathbf{q})}{\omega_j^2(\mathbf{q})}$$
$$\times \sum_{\mathbf{h}} \delta(\mathbf{Q} \pm \mathbf{q} - \mathbf{Q_h}), \qquad (4.1.3.6)$$

where $G_j(\mathbf{Q},\mathbf{q})$ is the 'structure factor for one-phonon scattering' by the mode $(j\mathbf{q})$ and is given by

$$G_j(\mathbf{Q},\mathbf{q}) = \sum_\kappa \frac{\mathbf{Q}\cdot\mathbf{e}(\kappa|j\mathbf{q})}{[m(\kappa)]^{1/2}} \cdot f_\kappa(\mathbf{Q})$$
$$\times \exp[i\mathbf{Q}\cdot\mathbf{r}(\kappa)] \exp(-W_\kappa).$$

The delta function in equation (4.1.3.6) implies that

$$\mathbf{Q} = \mathbf{Q_h} \pm \mathbf{q}, \qquad (4.1.3.7)$$

so that the scattering from the $3n$ modes with the same wavevector **q** is restricted to pairs of points in reciprocal space which are displaced by $\pm\mathbf{q}$ from the reciprocal-lattice points. (These satellite reflections are analogous to the pairs of 'ghosts' near the principal diffraction maxima in a grating ruled with a periodic error.) There is a huge number, N, of **q** vectors which are uniformly distributed throughout the Brillouin zone, and each of these vectors gives a cross section in accordance with equation (4.1.3.6). Thus the one-phonon TDS is spread throughout the whole of reciprocal space, rising to a maximum at the reciprocal-lattice points where $\omega \to 0$ for the acoustic modes.

For two-phonon scattering, involving modes with wavevectors $\mathbf{q}_1$ and $\mathbf{q}_2$, the scattering condition becomes

$$\mathbf{Q} = \mathbf{Q_h} \pm \mathbf{q}_1 \pm \mathbf{q}_2. \qquad (4.1.3.8)$$

The intensity at any point in reciprocal space is now contributed by a very large number of pairs of elastic waves with wavevectors satisfying equation (4.1.3.8). These vectors span the entire Brillouin zone, and so the variation of the two-phonon intensity with location in reciprocal space is less pronounced than for one-phonon scattering.

Expressions for $(d\sigma/d\Omega)^{(2)}$ and for higher terms in equation (4.1.3.2) will not be given, but a rough estimate of their relative magnitudes can be derived by using the Einstein model of the crystal. All frequencies are the same, $\omega_j(\mathbf{q}) = \omega_E$, and for one atom per cell ($n = 1$) the exponent of the temperature factor, equation (4.1.3.5), becomes

$$W = \frac{Q^2 k_B T}{2m\omega_E^2}, \qquad (4.1.3.9)$$

assuming classical equipartition of energy between modes: $E_j(\mathbf{q}) = k_B T$. The cross sections for zero-order, first-order, second-order . . . scattering are then

$$\left(\frac{d\sigma}{d\Omega}\right)^{(0)} = Nf^2 \exp(-2W)$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{(1)} = Nf^2 \exp(-2W)2W$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{(2)} = Nf^2 \exp(-2W)\frac{1}{2}(2W)^2$$

$$\vdots$$

and the total cross section is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = Nf^2 \exp(-2W)\left\{1 + 2W + \frac{1}{2}(2W)^2 + \frac{1}{6}(2W)^3 + \ldots\right\}.$$

The expression in curly brackets is the expansion of $\exp(2W)$. The nth term in the expansion, associated with the nth-order (n-phonon) process, is proportional to W^n or to $Q^{2n}T^n$. The higher-order processes are more important, therefore, at higher values of $(\sin\theta)/\lambda$ and at higher temperatures.

Our treatment so far applies to the TDS from single crystals. It can be extended to cover the TDS from polycrystalline samples, but the calculations are more complicated as the first-order scattering at a fixed value of $(\sin\theta)/\lambda$ is contributed by phonon wavevectors extending over the whole of the Brillouin zone. For a fuller discussion of the TDS from powders see Section 7.4.2 in *IT* C (1999).

4.1.4. Scattering of neutrons by thermal vibrations

The amplitude of the X-ray beam scattered by a single atom is denoted by the form factor or atomic scattering factor $f(\mathbf{Q})$. The corresponding quantity in neutron scattering is the scattering amplitude or scattering length b of an atom. b is independent of scattering angle and is also independent of neutron wavelength apart from for a few isotopes (*e.g.* ^{113}Cd, ^{149}Sm) with resonances in the thermal neutron region.

The scattering amplitude for atoms of the same chemical element can vary randomly from one atom to the next, as different amplitudes are associated with different isotopes. If the nucleus has a nonzero spin, even a single isotope has two different amplitudes, dependent on whether the nuclear spin is parallel or antiparallel to the spin of the incident neutron. If there is a variation in the amplitude associated with a particular type of atom, some of the waves scattered by the atom will interfere with one another and some will not. The first part is called coherent scattering and the second incoherent scattering. The amplitude of the coherent scattering is determined by the mean atomic scattering amplitude, averaged over the various isotopes and spin states of the atom, and is known as the coherent scattering length, $\bar{b}$.

A crucial difference between neutrons and X-rays concerns their energies:

$$E = \hbar^2 k^2/2m_n \quad \text{(neutrons)}$$
$$= c\hbar k \quad \text{(X-rays)},$$

where m_n is the neutron mass and c the velocity of light. At $\lambda = 1$ Å, neutrons have an energy of 0.08 eV or a temperature of about 800 K; for X-rays of this wavelength the corresponding temperature exceeds 10^8 K! Thermal neutrons have energies comparable with phonon energies, and so inelastic scattering processes, involving the exchange of energy between neutrons and phonons, produce appreciable changes in neutron energy. (These changes are readily determined from the change in wavelength or velocity of the scattered neutrons.) It is customary to refer to the thermal diffuse scattering of neutrons as 'inelastic neutron scattering' to draw attention to this energy change.

For a scattering process in which energy is exchanged with just one phonon, energy conservation gives

$$E_0 - E = \varepsilon\hbar\omega_j(\mathbf{q}), \tag{4.1.4.1}$$

where E_0 and E are the energies of the neutron before and after scattering. If $\varepsilon = +1$ the neutron loses energy by creating a phonon ('phonon emission'), and if $\varepsilon = -1$ it gains energy by annihilating a phonon ('phonon absorption').

The partial differential scattering cross section $\mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}\omega$ gives the probability that neutrons will be scattered into a small solid angle $\mathrm{d}\Omega$ about the direction $\mathbf{k}$ with a change of energy between $\hbar\omega$ and $\hbar(\omega + \mathrm{d}\omega)$. This cross section can be split into two terms, known as the coherent and incoherent cross sections:

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}} + \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{incoh}}.$$

The coherent cross section depends on the correlation between the positions of all the atoms at different times, and so gives interference effects. The incoherent cross section depends only on the correlation between the positions of the same atom at different times, giving no interference effects. Incoherent inelastic scattering is the basis of a powerful technique for studying the dynamics of molecular crystals containing hydrogen (Boutin & Yip, 1968).

The coherent scattering cross section $(\mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}\omega)_{\text{coh}}$ can be expanded, as in the X-ray case [equation (4.1.3.2)], into terms representing the contributions from zero-phonon, one-phonon, two-phonon ... scattering. To determine phonon dispersion relations, we measure the one-phonon contribution and this arises from both phonon emission and phonon absorption:

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}}^{(1)} = \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}+1}^{(1)} + \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}-1}^{(1)}.$$

The superscript (1) denotes a one-phonon process, and the subscript $+1$ (-1) indicates emission (absorption).

The emission cross section is given by (Squires, 1978)

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}+1}^{(1)} = \frac{\hbar k}{k_0}\frac{4\pi^3}{\mathrm{v}}\sum_{j\mathbf{q}}\sum_{\mathbf{Q_h}}\frac{[n_j(\mathbf{q}) + 1]}{\omega_j(\mathbf{q})}$$
$$\times \left|\frac{b_\kappa}{[m(\kappa)]^{1/2}}\exp[i\mathbf{Q}\cdot\mathbf{r}(\kappa)]\right.$$
$$\times \left.\mathbf{Q}\cdot\mathbf{e}(\kappa|j\mathbf{q})\exp(-W_\kappa)\right|^2$$
$$\times \delta[\omega - \omega_j(\mathbf{q})]\delta(\mathbf{Q} - \mathbf{Q_h} + \mathbf{q}),$$
$$\tag{4.1.4.2}$$

whereas for phonon absorption

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\text{coh}-1}^{(1)} = \frac{\hbar k}{k_0}\frac{4\pi^3}{\mathrm{v}}\sum_{j\mathbf{q}}\sum_{\mathbf{Q_h}}\frac{[n_j(\mathbf{q})]}{\omega_j(\mathbf{q})}$$
$$\times \left|\frac{b_\kappa}{[m(\kappa)]^{1/2}}\exp[i\mathbf{Q}\cdot\mathbf{r}(\kappa)]\right.$$
$$\times \left.\mathbf{Q}\cdot\mathbf{e}(\kappa|j\mathbf{q})\exp(-W_\kappa)\right|^2$$
$$\times \delta[\omega + \omega_j(\mathbf{q})]\delta(\mathbf{Q} - \mathbf{Q_h} - \mathbf{q}).$$
$$\tag{4.1.4.3}$$

The first delta function in these two expressions embodies energy conservation,

$$\hbar\omega \equiv \frac{\hbar^2}{2m_n}(k_0^2 - k^2) = \varepsilon\hbar\omega_j(\mathbf{q}),$$

and the second embodies conservation of momentum,

$$\mathbf{Q} \equiv \mathbf{k} - \mathbf{k}_0 = \mathbf{Q_h} - \varepsilon\mathbf{q}. \tag{4.1.4.4}$$

The phonon population number, $n_j(\mathbf{q})$, tends to zero as $T \to 0$ [see equation (4.1.2.6)], so that the one-phonon absorption cross