4. DIFFUSE SCATTERING AND RELATED TOPICS

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

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

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

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

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

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 $(d^2\sigma/d\Omega\, d\omega)_{\text{coh}}$ 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:

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

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)

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

whereas for phonon absorption

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

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,

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

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

section is very small at low temperatures where there are few phonons for the radiation to absorb. Comparison of equations (4.1.4.2) and (4.1.4.3) shows that there is always a greater probability that the neutrons are scattered with energy loss rather than with energy gain.

Normally it is not possible in X-ray experiments to distinguish between phonon emission and phonon absorption, and the measured cross section is obtained by summing over all energy transfers. The cross section for X-rays can be derived from the neutron formulae, equations (4.1.4.2) and (4.1.4.3), by putting $k = k_0$ and by replacing b_κ with $f_\kappa(\mathbf{Q})$. Integration over ω and addition of the parts for emission and absorption gives the X-ray formula (4.1.3.6).

The theory of neutron scattering can also be formulated in terms of thermal averages known as Van Hove correlation functions (Van Hove, 1954). For example, the partial differential cross section for coherent scattering is

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\mathrm{coh}} = \frac{k}{k_0} S(\mathbf{Q}, \omega),$$

where

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar} \int G(\mathbf{r}, t) \exp[i(\mathbf{Q}\cdot\mathbf{r} - \omega t)]\,\mathrm{d}\mathbf{r}\,\mathrm{d}t.$$

$S(\mathbf{Q}, \omega)$ is the Fourier transform in space and time of $G(\mathbf{r}, t)$, the time-dependent pair-correlation function. The classical interpretation of $G(\mathbf{r}, t)$ is that it is the probability of finding any atom at time t in a volume $\mathrm{d}\mathbf{r} = \mathrm{d}^3 r$, if there is an atom at the origin at time zero.

4.1.5. Phonon dispersion relations

Both X-rays and neutrons are used for determining crystal structures, but the X-ray method plays the dominant role. The reverse is true for the measurement of phonon dispersion relations: the experimental determination of $\omega(\mathbf{q})$ *versus* $\mathbf{q}$ was first undertaken with X-rays, but the method has been superseded by the technique of coherent inelastic neutron scattering (or neutron spectroscopy). For phonon wavevectors lying anywhere within the first Brillouin zone, it is necessary to employ radiation of wavelength comparable with interatomic distances and of energy comparable with lattice vibrational energies. X-rays satisfy the first of these conditions, but not the second, whereas the opposite holds for infrared radiation. Thermal neutrons satisfy both conditions simultaneously.

4.1.5.1. *Measurement with X-rays*

Frequencies can be derived indirectly with X-rays from the intensity of the thermal diffuse scattering. For a monatomic crystal with one atom per primitive cell, there are no optic modes and the one-phonon TDS intensity, equation (4.1.3.6), reduces to

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = Q^2 f^2 e^{-2W} \sum_{j=1}^{3} \frac{E_j(\mathbf{q})}{\omega^2(\mathbf{q})} \cos^2 \alpha_j(\mathbf{q}) \delta(\mathbf{Q} \pm \mathbf{q} - \mathbf{Q_h}), \quad (4.1.5.1)$$

where $\alpha_j(\mathbf{q})$ is the angle between $\mathbf{Q}$ and the direction of polarization of the mode ($j\mathbf{q}$). There are three acoustic modes associated with each wavevector $\mathbf{q}$, but along certain directions of $\mathbf{Q}$ it is possible to isolate the intensities contributed by the individual modes by choosing $\alpha_j(\mathbf{q})$ to be close to 0 or 90°. Equation (4.1.5.1) can then be employed to derive the frequency $\omega_j(\mathbf{q})$ for just one mode. The measured intensity must be corrected for multi-phonon and Compton scattering, both of which can exceed the intensity of the one-phonon scattering. The correction for two-phonon scattering involves an integration over the entire Brillouin zone, and this in turn requires an approximate knowledge of the dispersion relations.

The correction for Compton scattering can be made by repeating the measurements at low temperature.

The X-ray method is hardly feasible for systems with several atoms in the primitive cell. It comes into its own for those few materials which cannot be examined by neutrons. These include boron, cadmium and samarium with high absorption cross sections for thermal neutrons, and vanadium with a very small coherent (and a large incoherent) cross section for the scattering of neutrons. An important feature of TDS measurements with X-rays is in providing an independent check on interatomic or intermolecular force constants derived from measurements with inelastic neutron scattering. The force model is used to generate phonon frequencies and eigenvectors, which are then employed to compute the one-phonon and multi-phonon contributions to the X-ray TDS. Any discrepancy between calculated and observed X-ray intensities might be ascribed to such features as ionic deformation (Buyers *et al.*, 1968) or anharmonicity (Schuster & Weymouth, 1971).

4.1.5.2. *Measurement with neutrons*

The inelastic scattering of neutrons by phonons gives rise to changes of energy which are readily measured and converted to frequencies $\omega_j(\mathbf{q})$ using equation (4.1.4.1). The corresponding wavevector $\mathbf{q}$ is derived from the momentum conservation relation (4.1.4.4). Nearly all phonon dispersion relations determined to date have been obtained in this way. Well over 200 materials have been examined, including half the chemical elements, a large number of alloys and diatomic compounds, and rather fewer molecular crystals (Dolling, 1974; Bilz & Kress, 1979). Phonon dispersion curves have been determined in crystals with up to ten atoms in the primitive cell, for example, tetracyanoethylene (Chaplot *et al.*, 1983).

The principal instrument for determining phonon dispersion relations with neutrons is the triple-axis spectrometer, first designed and built by Brockhouse (Brockhouse & Stewart, 1958). The modern instrument is unchanged apart from running continuously under computer control. A beam of thermal neutrons falls on a single-crystal monochromator, which Bragg reflects a single wavelength on to the sample in a known orientation. The magnitude of the scattered wavevector, and hence the change of energy on scattering by the sample, is found by measuring the Bragg angle at which the neutrons are reflected by the crystal analyser. The direction of $\mathbf{k}$ is defined by a collimator between the sample and analyser.

In the 'constant $\mathbf{Q}$' mode of operating the triple-axis spectrometer, the phonon wavevector is kept fixed while the energy transfer $\hbar\omega$ is varied. This allows the frequency spectrum to be determined for all phonons sharing the same $\mathbf{q}$; the spectrum will contain up to $3n$ frequencies, corresponding to the $3n$ branches of the dispersion relations.

In an inelastic neutron scattering experiment, where the TDS intensity is of the order of one-thousandth of the Bragg intensity, it is necessary to use a large sample with a volume of 1 cm^3, or more. The sample should have a high cross section for coherent scattering as compared with the cross sections for incoherent scattering and for true absorption. Crystals containing hydrogen should be deuterated.

Dolling (1974) has given a comprehensive review of the measurement of phonon dispersion relations by neutron spectroscopy.

4.1.5.3. *Interpretation of dispersion relations*

The usual procedure for analysing dispersion relations is to set up the Born–von Kármán formalism with interatomic force constants Φ. The calculated frequencies $\omega_j(\mathbf{q})$ are then derived from the eigenvalues of the dynamical matrix $\mathbf{D}$ (Section 4.1.2.1) and the force constants fitted, by least squares, to the observed frequencies. Several sets of force constants may describe the frequencies equally