

## 4.1. THERMAL DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{coh}}^{(1)} = \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{coh}+1}^{(1)} + \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{coh}-1}^{(1)}. \quad \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{coh}} = \frac{k}{k_0} S(\mathbf{Q}, \omega),$$

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)

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

whereas for phonon absorption

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

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,

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

The phonon population number,  $n_j(\mathbf{q})$ , tends to zero as  $T \rightarrow 0$  [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  $b_\kappa$  with  $f_\kappa(\mathbf{Q})$ . Integration over  $\omega$  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

where

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

$S(\mathbf{Q}, \omega)$  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  $d\mathbf{r} = d^3r$ , 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

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

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.

This 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

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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).

With the availability of dedicated beamlines at third-generation synchrotrons, inelastic X-ray scattering is an alternative method of determining phonon dispersion relations in crystals (Burkel, 2000). The basic design of the X-ray instrument is the same as the three-axis spectrometer for neutron scattering (see Section 4.1.5.2 below): however, it is necessary to measure the minute change in energy of the scattered X-rays to a resolution of a few meV. This *tour de force* is achieved by adopting some novel experimental procedures. These include the use of a monochromator and analyser of perfect silicon crystals, both of which are operated under extreme conditions of Bragg back reflection ( $\theta \simeq 89.95^\circ$ ). Also, energy scans are performed by varying the relative temperature (and thereby the relative lattice spacing) between the monochromator and analyser with millikelvin precision. The X-ray spot size is in the submillimetre range, and so very small samples can be examined. A good example of this X-ray method is the study by Ruf *et al.* (2001) of the optic and acoustic modes of GaN, which possesses the wurtzite structure: crystals of GaN are too small to be examined by the traditional neutron method.

### 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, tetra-cyanoethylene (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  $1\text{ cm}^3$ , 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 an assumed set of interatomic force constants  $\Phi$ . 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 well, and to decide which set is preferable it is necessary to compare eigenvectors as well as eigenvalues (Cochran, 1971).

The main interest in the curves is in testing different models of interatomic potentials, whose derivatives are related to the interatomic force constants. For the solid inert gases the curves are reproduced reasonably well using a two-parameter Lennard–Jones 6–12 potential, although calculated frequencies are systematically higher than the experimental points near the Brillouin-zone boundary (Fujii *et al.*, 1974). To reproduce the dispersion relations in metals it is necessary to use a large number of interatomic force constants, extending to at least fifth neighbours. The number of independent constants is then too large for a meaningful analysis with the Born–von Kármán theory, but in the pseudo-potential approximation (Harrison, 1966) only two parameters are required to give good agreement between calculated and observed frequencies of simple metals such as aluminium. In the rigid-ion model for ionic crystals, the ions are treated as point charges centred on the nuclei and polarization of the outermost electrons is ignored. This is unsatisfactory at high frequencies. In the shell model, polarization is accounted for by representing the ion as a rigid core connected by a flexible spring to a polarizable shell of outermost electrons. There are many variants of this model – extended shell, overlap shell, deformation dipole, breathing shell . . . (Bilz & Kress, 1979). For molecular crystals the contributions to the force constants from the intermolecular forces can be derived from the nonbonded atomic pair potential of, say, the 6-exponential type:

$$\varphi(r) = -\frac{A_{ij}}{r^6} + B_{ij} \exp(-C_{ij}r).$$

Here,  $i, j$  label atoms in different molecules. The values of the parameters  $A, B, C$  depend on the pair of atomic species  $i, j$  only. For hydrocarbons they have been tabulated for different atom pairs by Kitaigorodskii (1966) and Williams (1967). The 6-exponential potential is applicable to molecular crystals that are stabilized mainly by London–van der Waals interactions; it is likely to fail when hydrogen bonds are present.

### 4.1.6. Measurement of elastic constants

There is a close connection between the theory of lattice dynamics and the theory of elasticity. Acoustic modes of vibration of long wavelength propagate as elastic waves in a continuous medium, with all the atoms in one unit cell moving in phase with one another. These vibrations are sound waves with velocities which can be calculated from the macroscopic elastic constants and from the density. The sound velocities are also given by the slopes, at  $q = 0$ , of the acoustic branches of the phonon dispersion relations. A knowledge of the velocities, or of the elastic constants, is necessary in estimating the TDS contribution to measured Bragg intensities.

The elastic constants relate the nine components of stress and nine components of strain, making 81 constants in all. This large number is reduced to 36, because there are only six independent components of stress and six independent components of strain. An economy of notation is now possible, replacing the indices 11 by 1, 22 by 2, 33 by 3, 23 by 4, 31 by 5 and 12 by 6, so that the