

## 4.1. Thermal diffuse scattering of X-rays and neutrons

BY B. T. M. WILLIS

### 4.1.1. Introduction

Thermal motion of the atoms in a crystal gives rise to a reduction in the intensities of the Bragg reflections and to a diffuse distribution of non-Bragg scattering in the rest of reciprocal space. This distribution is known as thermal diffuse scattering (TDS). Measurement and analysis of TDS gives information about the lattice dynamics of the crystal, *i.e.* about the small oscillatory displacements of the atoms from their equilibrium positions which arise from thermal excitations. Lattice-dynamical models form the basis for interpreting many physical properties – for example, specific heat and thermal conductivity – which cannot be explained by a static model of the crystal.

Reference to a lattice-dynamical model is found in Newton's *Principia*, which contains a discussion of the vibrations of a linear chain of equidistant mass points connected by springs. The model was used to estimate the speed of sound in air. The vibrational properties of a one-dimensional crystal treated as a linear chain of atoms provide the starting point for several modern treatises on the lattice dynamics of crystals.

The classical theory of the dynamics of three-dimensional crystals is based on the treatment of Born & von Kármán (1912, 1913). In this theory, the restoring force on an atom is determined not by the displacement of the atom from its equilibrium position, but by its displacement relative to its neighbours. The atomic motion is then considered in terms of travelling waves, or 'lattice vibrations', extending throughout the whole crystal. These waves are the normal modes of vibration, in which each mode is characterized by a wavevector  $\mathbf{q}$ , an angular frequency  $\omega(\mathbf{q})$  and certain polarization properties.

For twenty years after its publication the Born–von Kármán treatment was eclipsed by the theory of Debye (1912). In the Debye theory the crystal is treated as a continuous medium instead of a discrete array of atoms. The theory gives a reasonable fit to the integral vibrational properties (for example, the specific heat or the atomic temperature factor) of simple monatomic crystals. It fails to account for the form of the frequency distribution function which relates the number of modes and their frequency.

An even simpler model than Debye's is due to Einstein (1907), who considered the atoms in the crystal to be vibrating independently of each other and with the same frequency  $\omega_E$ . By quantizing the energy of each atom in units of  $\hbar\omega_E$ , Einstein showed that the specific heat falls to zero at  $T = 0$  K and rises asymptotically to the Dulong and Petit value for  $T$  much larger than  $\hbar\omega_E/k_B$ . ( $\hbar$  is Planck's constant divided by  $2\pi$  and  $k_B$  is Boltzmann's constant.) His theory accounts satisfactorily for the breakdown of equipartition of energy at low temperatures, but it predicts a more rapid fall-off of specific heat with decreasing temperature than is observed.

Deficiencies in the Debye theory were noted by Blackman (1937), who showed that they are overcome satisfactorily using the more rigorous Born–von Kármán theory. Extensive X-ray studies of Laval (1939) on simple structures such as sylvine, aluminium and diamond showed that the detailed features of the TDS could only be explained in terms of the Born–von Kármán theory. The X-ray work on aluminium was developed further by Olmer (1948) and by Walker (1956) to derive the phonon dispersion relations (see Section 4.1.5) along various symmetry directions in the crystal.

It is possible to measure the vibrational frequencies directly with X-rays, but such measurements are very difficult as lattice vibrational energies are many orders of magnitude less than X-ray energies. The situation is much more favourable with thermal neutrons because their wavelength is comparable with interatomic spacings and their energy is comparable with a quantum of

vibrational energy (or phonon). The neutron beam is scattered inelastically by the lattice vibrations, exchanging energy with the phonons. By measuring the energy change for different directions of the scattered beam, the dispersion relations  $\omega(\mathbf{q})$  can be determined. Brockhouse & Stewart (1958) reported the first dispersion curves to be derived in this way; since then the neutron technique has become the principal experimental method for obtaining detailed information about lattice vibrations.

In this chapter we shall describe briefly the standard treatment of the lattice dynamics of crystals. There follows a section on the theory of the scattering of X-rays by lattice vibrations, and a similar section on the scattering of thermal neutrons. We then refer briefly to experimental work with X-rays and neutrons. The final section is concerned with the measurement of elastic constants: these constants are required in calculating the TDS correction to measured Bragg intensities (see Section 7.4.2 of *IT C*, 1999).

### 4.1.2. Dynamics of three-dimensional crystals

For modes of vibration of very long wavelength, the crystal can be treated as a homogeneous elastic continuum without referring to its crystal or molecular structure. The theory of the propagation of these elastic waves is based on Hooke's law of force and on Newton's equations of motion. As the wavelength of the vibrations becomes shorter and shorter and approaches the separation of adjacent atoms, the calculation of the vibrational properties requires a knowledge of the crystal structure and of the nature of the forces between adjacent atoms. The three-dimensional treatment is based on the formulation of Born and von Kármán, which is discussed in detail in the book by Born & Huang (1954) and in more elementary terms in the books by Cochran (1973) and by Willis & Pryor (1975).

Before setting up the equations of motion, it is necessary to introduce three approximations:

(i) *The harmonic approximation.* When an atom is displaced from its equilibrium position, the restoring force is assumed to be proportional to the displacement, measured relative to the neighbouring atoms. The approximation implies no thermal expansion and other properties not possessed by real crystals; it is a reasonable assumption in the lattice-dynamical theory provided the displacements are not too large.

(ii) *The adiabatic approximation.* We wish to set up a potential function for the crystal describing the binding between the atoms. However, the binding involves electronic motions whereas the dynamics involve nuclear motions. The adiabatic approximation, known as the Born–Oppenheimer approximation in the context of molecular vibrations, provides the justification for adopting the same potential function to describe both the binding and the dynamics. Its essence is that the electronic and nuclear motions may be considered separately. This is possible if the nuclei move very slowly compared with the electrons: the electrons can then instantaneously take up a configuration appropriate to that of the displaced nuclei without changing their quantum state. The approximation holds well for insulators, where electronic transition energies are high owing to the large energy gap between filled and unfilled electron states. Surprisingly, it even works for metals, because (on account of the Pauli principle) only a few electrons near the Fermi level can make transitions.

(iii) *Periodic boundary conditions.* These are introduced to avoid problems associated with the free surface. The system is treated as an infinite crystal made up of contiguous, repeating blocks of the actual crystal. The periodic (or cyclic) boundary conditions require that the displacements of corresponding atoms in different blocks are identical. The validity of the conditions was challenged by

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

Raman (1941), but these objections were safely disposed of by Ledermann (1944).

##### 4.1.2.1. Equations of motion

As a result of thermal fluctuations, the atoms vibrate about their equilibrium positions, so that the actual position of the  $\kappa$ th atom in the  $l$ th primitive cell is given by

$$\mathbf{R}(\kappa l) = \mathbf{r}(\kappa l) + \mathbf{u}(\kappa l)$$

with  $\mathbf{r}$  representing the equilibrium position and  $\mathbf{u}$  the thermal displacement. (In lattice-dynamical theory it is advantageous to deal with the primitive cell, as it possesses the fewest degrees of freedom.) The kinetic energy of the vibrating crystal is

$$(1/2) \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l),$$

where  $m(\kappa)$  is the mass of atom  $\kappa$  and the index  $\alpha$  ( $\alpha = 1, 2, 3$ ) refers to the Cartesian components of the displacement. (The dot denotes the time derivative.)

If the adiabatic approximation is invoked, the potential energy  $V$  of the crystal can be expressed as a function of the instantaneous atomic positions. Expanding  $V$  in powers of  $\mathbf{u}(\kappa l)$ , using the three-dimensional form of Taylor's series, we have

$$V = V^{(0)} + V^{(1)} + V^{(2)} + V^{(3)} + \dots,$$

where  $V^{(0)}$  is the static (equilibrium) potential and  $V^{(1)}$ ,  $V^{(2)}$  are given by

$$V^{(1)} = \sum_{\kappa l \alpha} \left. \frac{\partial V}{\partial u_{\alpha}(\kappa l)} \right|_0 u_{\alpha}(\kappa l)$$

$$V^{(2)} = \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0 u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l').$$

The subscript zero indicates that the derivatives are to be evaluated at the equilibrium configuration. In the harmonic approximation,  $V^{(3)}$  and all higher terms in the expansion are neglected.

At equilibrium the forces on an atom must vanish, so that

$$V^{(1)} = 0.$$

Ignoring the static potential  $V^{(0)}$ , the quadratic term  $V^{(2)}$  only remains and the Hamiltonian for the crystal (the sum of the kinetic and potential energies) is then

$$H = \frac{1}{2} \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l)$$

$$+ \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l'),$$

(4.1.2.1)

where  $\Phi_{\alpha \alpha'}$  is an element of the  $3 \times 3$  'atomic force-constant matrix' and is defined (for distinct atoms  $\kappa l$ ,  $\kappa' l'$ ) by

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} = \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0.$$

It is the negative of the force in the  $\alpha$  direction imposed on the atom ( $\kappa l$ ) when atom ( $\kappa' l'$ ) is displaced unit distance along  $\alpha'$  with all the remaining atoms fixed at their equilibrium sites.  $\Phi_{\alpha \alpha'}$  is defined differently for the self-term with  $\kappa = \kappa'$  and  $l = l'$ :

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa \\ l & l \end{pmatrix} = - \sum_{\substack{\kappa l \\ \kappa l' \neq \kappa l}} \sum_{\substack{\kappa' l' \\ \kappa l' \neq \kappa l}} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix}.$$

Thus the self-matrix describes the force on ( $\kappa l$ ) when the atom itself is displaced with all the remaining atoms kept stationary.

There are restrictions on the number of distinct force constants  $\Phi_{\alpha \alpha'}$ : these are imposed by symmetry and by the requirement that the potential energy is invariant under infinitesimal translations and rotations of the rigid crystal. Such constraints are discussed in the book by Venkataraman *et al.* (1975).

Applying Hamilton's equations of motion to equation (4.1.2.1) now gives

$$m(\kappa) \ddot{u}_{\alpha}(\kappa l) = - \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha'}(\kappa' l').$$

(4.1.2.2)

These represent  $3nN$  coupled differential equations, where  $n$  is the number of atoms per primitive cell ( $\kappa = 1, \dots, n$ ) and  $N$  is the number of cells per crystal ( $l = 1, \dots, N$ ).

By applying the periodic boundary conditions, the solutions of equation (4.1.2.2) can be expressed as running, or travelling, plane waves extending throughout the entire crystal. The number of independent waves (or normal modes) is  $3nN$ . Effectively, we have transferred to a new coordinate system: instead of specifying the motion of the individual atoms, we describe the thermal motion in terms of normal modes, each of which contributes to the displacement of each atom. The general solution for the  $\alpha$  component of the displacement of ( $\kappa l$ ) is then given by the superposition of the displacements from all modes:

$$u_{\alpha}(\kappa l) = [m(\kappa)]^{-1/2} \sum_{j \mathbf{q}} |A_j(\mathbf{q})| e_{\alpha}(\kappa | j \mathbf{q})$$

$$\times \exp\{i[\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}.$$

(4.1.2.3)

Here  $\mathbf{q}$  is the wavevector of a mode (specifying both its wavelength and direction of propagation in the crystal) and  $\omega(\mathbf{q})$  its frequency. There are  $N$  distinct wavevectors, occupying a uniformly distributed mesh of  $N$  points in the Brillouin zone (reciprocal cell); each wavevector is shared by  $3n$  modes which possess, in general, different frequencies and polarization properties. Thus an individual mode is conveniently labelled ( $j \mathbf{q}$ ), where  $j$  is an index ( $j = 1, \dots, 3n$ ) indicating the *branch*. The scalar quantity  $|A_j(\mathbf{q})|$  in equation (4.1.2.3) is the amplitude of excitation of ( $j \mathbf{q}$ ) and  $e_{\alpha}(\kappa | j \mathbf{q})$  is the element of the eigenvector  $\mathbf{e}(j \mathbf{q})$  referring to the displacement in the  $\alpha$  direction of the atom  $\kappa$ . The eigenvector itself, with dimensions  $n \times 1$ , determines the pattern of atomic displacements in the mode ( $j \mathbf{q}$ ) and its magnitude is fixed by the orthonormality and closure conditions

$$\sum_{\alpha \kappa} e_{\alpha}^*(\kappa | j \mathbf{q}) e_{\alpha}(\kappa | j' \mathbf{q}) = \delta_{jj'}$$

and

$$\sum_j e_{\alpha}(\kappa | j \mathbf{q}) e_{\alpha'}^*(\kappa' | j \mathbf{q}) = \delta_{\alpha \alpha'} \delta_{\kappa \kappa'}$$

with \* indicating complex conjugate and  $\delta$  the Kronecker delta.

The pre-exponential, or amplitude, terms in (4.1.2.3) are independent of the cell number. This follows from Bloch's (1928) theorem which states that, for corresponding atoms in different cells, the motions are identical as regards their amplitude and direction and differ only in phase. The theorem introduces an enormous simplification as it allows us to restrict attention to the  $3n$  equations of motion of the  $n$  atoms in just one cell, rather than the  $3nN$  equations of motion for all the atoms in the crystal.

Substitution of (4.1.2.3) into (4.1.2.2) gives the equations of motion in the form

$$\omega_j^2(\mathbf{q}) e_{\alpha}(\kappa | j \mathbf{q}) = \sum_{\alpha' \kappa'} D_{\alpha \alpha'}(\kappa \kappa' | \mathbf{q}) e_{\alpha'}(\kappa' | j \mathbf{q}),$$

(4.1.2.4)

in which  $D_{\alpha \alpha'}$  is an element of the dynamical matrix  $\mathbf{D}(\mathbf{q})$ .  $D_{\alpha \alpha'}$  is

defined by

$$D_{\alpha\alpha'}(\kappa\kappa'|\mathbf{q}) = [m(\kappa)m(\kappa')]^{-1/2} \exp\{i\mathbf{q}[r(\kappa') - r(\kappa)]\} \\ \times \sum \Phi_{\alpha\alpha'} \begin{pmatrix} \kappa & \kappa' \\ 0 & L \end{pmatrix} \exp[i\mathbf{q} \cdot \mathbf{r}(L)], \quad (4.1.2.5)$$

where  $\mathbf{r}(\kappa)$  is the position of atom  $\kappa$  with respect to the cell origin,  $L$  is  $l' - l$  and  $\mathbf{r}(L)$  is the separation between cells  $l$  and  $l'$ . The element  $D_{\alpha\alpha'}$  is obtained by writing down the  $\alpha\alpha'$  component of the force constant between atoms  $\kappa, \kappa'$  which are  $L$  cells apart and multiplying by the phase factor  $\exp[i\mathbf{q} \cdot \mathbf{r}(L)]$ ; this term is then summed over those values of  $L$  covering the range of interaction of  $\kappa$  and  $\kappa'$ .

The dynamical matrix is Hermitian and has dimensions  $3n \times 3n$ . Its eigenvalues are the squared frequencies  $\omega_j^2(\mathbf{q})$  of the normal modes and its eigenvectors  $\mathbf{e}(j\mathbf{q})$  determine the corresponding pattern of atomic displacements. The frequencies of the modes in three of the branches,  $j$ , go to zero as  $\mathbf{q}$  approaches zero: these are the acoustic modes. The remaining  $3n - 3$  branches contain the optic modes. There are  $N$  distinct  $\mathbf{q}$  vectors, and so, in all, there are  $3N$  acoustic modes and  $(3n - 3)N$  optic modes. Thus copper has acoustic modes but no optic modes, silicon and rock salt have an equal number of both, and lysozyme possesses predominantly optic modes.

#### 4.1.2.2. Quantization of normal modes. Phonons

Quantum concepts are not required in solving the equations of motion (4.1.2.4) to determine the frequencies and displacement patterns of the normal modes. The only place where quantum mechanics is necessary is in calculating the energy of the mode, and from this the amplitude of vibration  $|A_j(\mathbf{q})|$ .

It is possible to discuss the theory of lattice dynamics from the beginning in the language of quantum mechanics (Donovan & Angress, 1971). Instead of treating the modes as running waves, they are conceived as an assemblage of indistinguishable quasi-particles called phonons. Phonons obey Bose–Einstein statistics and are not limited in number. The number of phonons, each with energy  $\hbar\omega_j(\mathbf{q})$  in the vibrational state specified by  $\mathbf{q}$  and  $j$ , is given by

$$n_j(\mathbf{q}) = \{\exp[\hbar\omega_j(\mathbf{q})/k_B T] - 1\}^{-1} \quad (4.1.2.6)$$

and the mode energy  $E_j(\mathbf{q})$  by

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})[n_j(\mathbf{q}) + (1/2)]. \quad (4.1.2.7)$$

Thus the quantum number  $n_j(\mathbf{q})$  describes the degree of excitation of the mode ( $j\mathbf{q}$ ). The relation between  $E_j(\mathbf{q})$  and the amplitude  $|A_j(\mathbf{q})|$  is

$$E_j(\mathbf{q}) = N\omega_j^2(\mathbf{q})|A_j(\mathbf{q})|^2. \quad (4.1.2.8)$$

Equations (4.1.2.6) to (4.1.2.8) together determine the value of  $|A_j(\mathbf{q})|$  to be substituted into equation (4.1.2.3) to give the atomic displacement in terms of the absolute temperature and the properties of the normal modes.

In solving the lattice-dynamical problem using the Born–von Kármán analysis, the first step is to set up a force-constant matrix describing the interactions between all pairs of atoms. This is followed by the assembly of the dynamical matrix  $\mathbf{D}$ , whose eigenvalues give the frequencies of the normal modes and whose eigenvectors determine the patterns of atomic displacement for each mode.

Before considering the extension of this treatment to molecular crystals, we shall comment briefly on the less rigorous treatments of Einstein and Debye.

#### 4.1.2.3. Einstein and Debye models

In the Einstein model it is assumed that each atom vibrates in its private potential well, entirely unaffected by the motion of its neighbours. There is no correlation between the motion of different atoms, whereas correlated motion – in the form of collective modes propagating throughout the crystal – is a central feature in explaining the characteristics of the TDS. Nevertheless, the Einstein model is occasionally used to represent modes belonging to flat optic branches of the dispersion relations, with the frequency written symbolically as  $\omega(\mathbf{q}) = \omega_E$  (constant).

In the Debye model the optic branches are ignored. The dispersion relations for the remaining three acoustic branches are assumed to be the same and represented by

$$\omega(\mathbf{q}) = \mathbf{v}_s q, \quad (4.1.2.9)$$

where  $\mathbf{v}_s$  is a mean sound velocity. The Brillouin zone is replaced by a sphere with radius  $q_D$  chosen to ensure the correct number of modes. The linear relationship (4.1.2.9) holds right up to the boundary of the spherical zone. In an improved version of the Debye model, (4.1.2.9) is replaced by the expression

$$\omega(\mathbf{q}) = \mathbf{v}_s(2q_D/\pi) \sin(\pi q/2q_D), \quad (4.1.2.10)$$

which is the same as (4.1.2.9) at  $q = 0$  but gives a sinusoidal dispersion relation with zero slope at the zone boundary.

#### 4.1.2.4. Molecular crystals

The full Born–von Kármán treatment becomes excessively cumbersome when applied to most molecular crystals. For example, for naphthalene with two molecules or 36 atoms in the primitive cell, the dynamical matrix has dimensions  $108 \times 108$ . Moreover, the physical picture of molecules or of groups of atoms, vibrating in certain modes as quasi-rigid units, is lost in the full treatment.

To simplify the setting up of the dynamical matrix, it is assumed that the molecules vibrate as rigid units in the crystal with each molecule possessing three translational and three rotational (librational) degrees of freedom. The motion of these rigid groups as a whole is described by the *external modes* of motion, whereas the *internal modes* arise from distortions within an individual group. The frequencies of these internal modes, which are largely determined by the strong intramolecular forces, are unaffected by the phase of the oscillation between neighbouring cells: the modes are taken, therefore, to be equivalent to those of the free molecule. The remaining external modes are calculated by applying the Born–von Kármán procedure to the crystal treated as an assembly of rigid molecules.

The dynamical matrix  $\mathbf{D}(\mathbf{q})$  now has dimensions  $6n' \times 6n'$ , where  $n'$  is the number of molecules in the primitive cell: for naphthalene,  $\mathbf{D}$  is reduced to  $12 \times 12$ . The elements of  $\mathbf{D}$  can be expressed in the same form as equation (4.1.2.5) for an atomic system.  $\kappa, \kappa'$  refer to molecules which are  $L$  cells apart and the indices  $\alpha, \alpha' (= 1, \dots, 6)$  label the six components of translation and rotation.  $m(\kappa)$  in equation (4.1.2.5) is replaced by  $m_\alpha(\kappa)$  where  $m_\alpha$  represents the  $3 \times 3$  molecular-mass matrix for  $\alpha = 1, 2, 3$  and the  $3 \times 3$  moment-of-inertia matrix referred to the principal axes of inertia for  $\alpha = 4, 5, 6$ . The  $6 \times 6$  force-torque constant matrices  $\Phi_{\alpha\alpha'}$  are derived by taking the second derivative of the potential energy of the crystal with respect to the coordinates of translation and rotation.

#### 4.1.3. Scattering of X-rays by thermal vibrations

The change of frequency, or energy, of X-rays on being scattered by thermal waves is extremely small. The differential scattering cross section,  $d\sigma/d\Omega$ , giving the probability that X-rays are scattered into the solid angle  $d\Omega$  is then