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 give 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 ω_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 2π 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*, 2004).

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 Raman (1941*a,b*), 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 κth atom in the lth 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 κ and the index α (α = 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

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

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

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 3×3 'atomic force-constant matrix' and is defined (for distinct atoms κl, $\kappa' l'$) by

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

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

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

Thus the self-matrix describes the force on (κl) 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

$$m(\kappa)\ddot{u}_\alpha(\kappa l) = -\sum_{\kappa' l' \alpha'} \Phi_{\alpha\alpha'}\begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha'}(\kappa' l'). \qquad (4.1.2.2)$$

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 α component of the displacement of (κl) is then given by the superposition of the displacements from all modes:

$$u_\alpha(\kappa l) = [m(\kappa)]^{-1/2} \sum_{j\mathbf{q}} |A_j(\mathbf{q})|e_\alpha(\kappa|j\mathbf{q})$$
$$\times \exp\{i[\mathbf{q}\cdot\mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}. \qquad (4.1.2.3)$$

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 α direction of the atom κ. 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 δ 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

$$\omega_j^2(\mathbf{q})e_\alpha(\kappa|j\mathbf{q}) = \sum_{\alpha'\kappa'} D_{\alpha\alpha'}(\kappa\kappa'|\mathbf{q})e_{\alpha'}(\kappa'|j\mathbf{q}), \qquad (4.1.2.4)$$

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

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

where $\mathbf{r}(\kappa)$ is the position of atom κ 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 κ, κ' 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 κ and κ'.

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

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

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

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

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

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

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

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

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

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

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 108×108. 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 12×12. The elements of $\mathbf{D}$ can be expressed in the same form as equation (4.1.2.5) for an atomic system. κ, κ' refer to molecules which are L cells apart and the indices $\alpha, \alpha' (= 1, \ldots, 6)$ label the six components of translation and rotation. $m(\kappa)$ in equation (4.1.2.5) is replaced by $m_\alpha(\kappa)$ where m_α represents the 3×3 molecular-mass matrix for $\alpha = 1, 2, 3$ and represents the 3×3 moment-of-inertia matrix referred to the principal axes of inertia for $\alpha = 4, 5, 6$. The 6×6 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

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

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. $\mathbf{Q}$ is the 'scattering vector' defined by

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

where $\mathbf{k}$ and $\mathbf{k}_0$ are the wavevectors (each of magnitude $2\pi/\lambda$) of the scattered and incident beams, respectively. For Bragg scattering the magnitude of $\mathbf{Q}$ is $4\pi(\sin\theta)/\lambda$, where θ is the Bragg angle. $f_\kappa(\mathbf{Q})$ 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

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

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 $\mathbf{h}$ 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

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

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 $\mathbf{q}$ 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 $\mathbf{q}$ 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

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

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

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

$$\vdots$$

and the total cross section is

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

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* (2004).

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 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 atoms 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:

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

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 and $\varepsilon = \pm 1$. 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:

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

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

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

whereas for phonon absorption

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

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

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

where

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

$S(\mathbf{Q}, \omega)$ 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 multiphonon 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

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 ($\theta \simeq 89.95°$). Also, energy scans are performed by varying the relative temperature (and thereby the relative lattice spacing) between the monochromator and analyser with milli-kelvin 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 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 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

elastic constants are represented by c_{ij} with $i, j = 1, \ldots, 6$. Applying the principle of conservation of energy gives

$$c_{ij} = c_{ji}$$

and the number of constants is reduced further to 21. Crystal symmetry effects yet a further reduction. For cubic crystals there are just three independent constants (c_{11}, c_{12}, c_{44}) and the 6×6 matrix of elastic constants is

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix}.$$

In principle, the elastic constants can be derived from static measurements of the four quantities – compressibility, Poisson's ratio, Young's modulus and rigidity modulus. The measurements are made along different directions in the crystal: at least six directions are needed for the orthorhombic system. The accuracy of the static method is limited by the difficulty of measuring small strains.

Dynamic methods are more accurate as they depend on measuring a frequency or velocity. For a cubic crystal, the three elastic constants can be derived from the three sound velocities propagating along the single direction [110]; for non-cubic crystals the velocities must be measured along a number of non-equivalent directions.

Sound velocities can be determined in a number of ways. In the ultrasonic pulse technique, a quartz transducer sends a pulse through the crystal; the pulse is reflected from the rear surface back to the transducer, and the elapsed time for the round trip of several cm is measured. Brillouin scattering of laser light is also used (Vacher & Boyer, 1972). Fluctuations in dielectric constant caused by (thermally excited) sound waves give rise to a Doppler shift of the light frequency. The sound velocity is readily calculated from this shift, and the elastic constants are then obtained from the velocities along several directions, using the Christoffel relations (Hearmon, 1956). The Brillouin method is restricted to transparent materials. This restriction does not apply to neutron diffraction methods, which employ the inelastic scattering of neutrons (Willis, 1986; Schofield & Willis, 1987; Popa & Willis, 1994).

Tables of elastic constants of cubic and non-cubic crystals have been compiled by Hearmon (1946, 1956) and by Huntingdon (1958).

References

Bilz, H. & Kress, W. (1979). *Phonon Dispersion Relations in Insulators.* Berlin: Springer-Verlag.

Blackman, M. (1937). *On the vibrational spectrum of a three-dimensional lattice. Proc. R. Soc. London Ser. A*, **159**, 416–431.

Bloch, F. (1928). *Über die Quantenmechanik der Elektronen in Kristallgittern. Z. Phys.* **52**, 555–600.

Born, M. & Huang, K. (1954). *The Dynamical Theory of Crystal Lattices.* Oxford: Clarendon Press.

Born, M. & von Kármán, T. (1912). *Über Schwingungen in Raumgittern. Phys. Z.* **13**, 279–309.

Born, M. & von Kármán, T. (1913). *Zur Theorie der spezifischen Wärme. Phys. Z.* **14**, 15–19.

Boutin, H. & Yip, S. (1968). *Molecular Spectroscopy with Neutrons.* Cambridge: MIT Press.

Brockhouse, B. N. & Stewart, A. T. (1958). *Normal modes of aluminum by neutron spectrometry. Rev. Mod. Phys.* **30**, 236–249.

Burkel, E. (2000). *Phonon spectroscopy and inelastic X-ray scattering. Rep. Prog. Phys.* **63**, 171–232.

Buyers, W. J. L., Pirie, J. D. & Smith, T. (1968). *X-ray scattering from deformable ions. Phys. Rev.* **165**, 999–1005.

Chaplot, S. L., Mierzejewski, A., Pawley, G. S., Lefebvre, J. & Luty, T. (1983). *Phonon dispersion of the external and low-frequency internal vibrations in monoclinic tetracyanoethylene. J. Phys. C*, **16**, 625–644.

Cochran, W. (1971). *The relation between phonon frequencies and interatomic force constants. Acta Cryst.* A**27**, 556–559.

Cochran, W. (1973). *The Dynamics of Atoms in Crystals.* London: Edward Arnold.

Debye, P. (1912). *Zur Theorie der spezifischen Wärme. Ann. Phys. (Leipzig)*, **39**, 789–839.

Dolling, C. (1974). *Dynamical Properties of Solids*, Vol. 1, edited by G. K. Horton & A. A. Maradudin, pp. 541–629. Amsterdam: North-Holland.

Donovan, B. & Angress, J. F. (1971). *Lattice Vibrations.* London: Chapman and Hall.

Einstein, A. (1907). *Die Plancksche Theorie der Strahlung und die Theorie der spezifisichen Wärme. Ann. Phys. (Leipzig)*, **22**, 180–190, 800.

Fujii, Y., Lurie, N. A., Pynn, R. & Shirane, G. (1974). *Inelastic neutron scattering from solid ^{36}Ar. Phys. Rev. B*, **10**, 3647–3659.

Harrison, W. A. (1966). *Phonons in Perfect Lattices*, edited by R. W. H. Stevenson, pp. 73–109. Edinburgh: Oliver & Boyd.

Hearmon, R. F. S. (1946). *The elastic constants of anisotropic materials. Rev. Mod. Phys.* **18**, 409–440.

Hearmon, R. F. S. (1956). *The elastic constants of anisotropic materials. II. Adv. Phys.* **5**, 323–382.

Huntingdon, H. B. (1958). *The elastic constants of crystals. Solid State Phys.* **7**, 213–351.

International Tables for Crystallography (2004). Vol. C. *Mathematical, Physical and Chemical Tables*, edited by E. Prince. Dordrecht: Kluwer Academic Publishers.

Kitaigorodskii, A. J. (1966). *Empilement des molécules dans un cristal, potentiel d'interaction des atomes non liés par des liaisons de valence, et calcul du mouvement des molécules. J. Chim. Phys.* **63**, 8–16.

Laval, J. (1939). *Etude éxperimentale de la diffusion des rayons X par les cristaux. Bull. Soc. Fr. Minéral.* **62**, 137–253.

Ledermann, W. (1944). *Asymptotic formulae relating to the physical theory of crystals. Proc. R. Soc. London Ser. A*, **82**, 362–377.

Olmer, P. (1948). *Dispersion des vitesses des ondes acoustiques dans l'aluminium. Acta Cryst.* **1**, 57–63.

Popa, N. C. & Willis, B. T. M. (1994). *Thermal diffuse scattering in time-of-flight neutron diffractometry. Acta Cryst.* A**50**, 57–63.

Raman, C. V. (1941a). *The quantum theory of X-ray reflection. Proc. Indian Acad. Sci. Sect. A*, **14**, 317–376.

Raman, C. V. (1941b). *The thermal energy of crystalline solids: basic theory. Proc. Indian Acad. Sci. Sect. A*, **14**, 459–467.

Ruf, T., Serrano, J., Cardona, M., Pavone, P., Pabst, M., Krisch, M., D'Astuto, M., Suski, T., Grzegory, I. & Leszczynski, M. (2001). *Phonon dispersion curve in wurtzite-structure GaN determined by inelastic x-ray scattering. Phys. Rev. Lett.* **86**, 906–909.

Schofield, P. & Willis, B. T. M. (1987). *Thermal diffuse scattering in time-of-flight neutron diffraction. Acta Cryst.* A**43**, 803–809.

Schuster, S. L. & Weymouth, J. W. (1971). *Study of thermal diffuse X-ray scattering from lead single crystals. Phys. Rev. B*, **3**, 4143–4153.

Squires, G. L. (1978). *Introduction to the Theory of Thermal Neutron Scattering.* Cambridge University Press.

Vacher, R. & Boyer, L. (1972). *Brillouin scattering: a tool for the measurement of elastic and photoelastic constants. Phys. Rev. B*, **6**, 639–673.

Van Hove, L. (1954). *Correlations in space and time and Born approximation scattering in systems of interacting particles. Phys. Rev.* **95**, 249–262.

Venkataraman, G., Feldkamp, L. A. & Sahni, V. C. (1975). *Dynamics of Perfect Crystals.* Cambridge: MIT Press.

Walker, C. B. (1956). *X-ray study of lattice vibrations in aluminum. Phys. Rev.* **103**, 547–557.

Williams, D. E. (1967). *Non-bonded potential parameters derived from crystalline hydrocarbons. J. Chem. Phys.* **47**, 4680–4684.

Willis, B. T. M. (1986). *Determination of the velocity of sound in crystals by time-of-flight neutron diffraction. Acta Cryst.* A**42**, 514–525.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge University Press.

references