4. DIFFUSE SCATTERING AND RELATED TOPICS

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 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).

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