4. DIFFUSE SCATTERING AND RELATED TOPICS

can be separated by purely elastic neutron methods within the limits given by the energy resolution of an instrument. This technique is of particular importance at higher temperatures where TDS becomes remarkably strong. Neutron scattering is a good tool only in cases where (isotope/spin-)incoherent scattering is not too strong. In the case of magnetic materials confusion with paramagnetic diffuse scattering could occur. This is also important when electrons are trapped by defects which themselves act as paramagnetic centres.

As mentioned in Section 4.2.4.4.4 the evaluations of the γ, δ, ε depend on the assumption that the f's do not depend on $|\mathbf{H}|$ strongly within the range of measurement. Owing to the atomic form factor, this is not always well approximated in the X-ray case and is one of the main sources of error in the determination of the short-range-order parameters.

4.2.4.4.10. *Dynamic properties of defects*

Some brief remarks concerning the dynamic properties of defects as discussed in the previous sections now follow. Mass defects (impurity atoms), force-constant defects *etc.* influence the dynamic properties of the undistorted lattice and one could think of a modified TDS as discussed in Chapter 4.1. In the case of low defect concentrations special vibrational modes characterized by large amplitudes at the defect with frequency shifts and reduced lifetimes (resonant modes) or vibrational modes localized in space may occur. Other modes with frequencies near these particular modes may also be affected. Owing to the very low intensity of these phenomena their influence on the normal TDS is negligible and may be neglected in diffuse-scattering work. Theoretical treatments of crystals with higher defect concentrations are extremely difficult and not developed so far. For further reading see Böttger (1983).

4.2.4.5. *Orientational disorder*

Molecular crystals show in principle disorder phenomena similar to those discussed in previous sections (substitutional or displacement disorder). Here we have to replace the structure factors $F_\nu(\mathbf{H})$, used in the previous sections, by the molecular structure factors in their various orientations. Usually these are rapidly varying functions in reciprocal space which may obscure the disorder diffuse scattering. Disorder in molecular crystals is treated by Guinier (1963), Amorós & Amorós (1968), Flack (1970), Epstein *et al.* (1982), Welberry & Siripitayananon (1986, 1987), and others.

A particular type of disorder is very common in molecular and also in ionic crystals: the centres of masses of molecules or ionic complexes form a perfect 3D lattice but their orientations are disordered. Sometimes these solids are called plastic crystals. For comparison, the liquid-crystalline state is characterized by an orientational order in the absence of long-range positional order of the centres of the molecules. A clear-cut separation is not possible in cases where translational symmetry occurs in low dimension, *e.g.* in sheets or parallel to a few directions in crystal space. For discussion of these mesophases see Chapter 4.4.

An orientationally disordered crystal may be imagined in a static picture by freezing molecules in different sites in one of several orientations. Local correlations between neighbouring molecules and correlations between position and orientation may be responsible for orientational short-range order. Often thermal reorientations of the molecules are related to an orientationally disordered crystal. Thermal vibrations of the centres of masses of the molecules, librational or rotational excitations around one or more axes of the molecules, jumps between different equilibrium positions or diffusion-like phenomena are responsible for diffuse scattering of dynamic origin. As mentioned above the complexity of molecular structures and the associated large number of thermal modes complicate a separation from static disorder effects.

Generally high Debye–Waller factors are typical for scattering of orientationally disordered crystals. Consequently only a few Bragg reflections are observable. A large amount of structural information is stored in the diffuse background. It has to be analysed with respect to an incoherent and coherent part, elastic, quasielastic or inelastic nature, short-range correlations within one and the same molecule and between orientations of different molecules, and cross correlations between positional and orientational disorder scattering. Combined X-ray and neutron methods are therefore highly recommended.

4.2.4.5.1. *General expressions*

On the assumption of a well ordered 3D lattice, a general expression for the scattering by an orientationally disordered crystal with one molecule per unit cell may be given. This is a very common situation. Moreover, orientational disorder is frequently related to molecules with an overall 'globular' shape and consequently to crystals of high (in particular, averaged) spherical symmetry. In the following the relevant equations are given for this situation; these are discussed in some detail in a review article by Fouret (1979). The orientation of a molecule is characterized by a parameter ω_l, *e.g.* the set of Eulerian angles of three molecular axes with respect to the crystal axes: $\omega_l = 1, \ldots, D$ (D possible different orientations). The equilibrium position of the centre of mass of a molecule in orientation ω_l is given by $\mathbf{r}_l$, the equilibrium position of atom k within a molecule l in orientation ω_l by $\mathbf{r}_{lk}$ and a displacement from this equilibrium position by $\mathbf{u}_{lk}$. Averaging over a long time, *i.e.* supposing that the lifetime of a discrete configuration is long compared with the period of atomic vibrations, the observed intensity may be deduced from the intensity expression corresponding to a given configuration at time t:

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} F_l(\mathbf{H}, t) F_{l'}^+(\mathbf{H}, t)$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \tag{4.2.4.85}$$
$$F_l(\mathbf{H}, t) = \sum_k f_k \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} + \mathbf{u}_{lk})\}. \tag{4.2.4.86}$$

Averaging procedures must be carried out with respect to the thermal vibrations (denoted by an overbar) and over all configurations (symbol $\langle\ \rangle$). The centre-of-mass translational vibrations and librations of the molecules are most important in this context. (Internal vibrations of the molecules are assumed to be decoupled and remain unconsidered.)

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} \langle \overline{F_l(\mathbf{H}, t) F_{l'}^+(\mathbf{H}, t)} \rangle$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \tag{4.2.4.85a}$$

Thermal averaging gives (*cf.* Chapter 4.1)

$$I = \sum_l \sum_{l'} \overline{F_l F_{l'}^+} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}$$

$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}$$
$$\times \overline{\exp\{2\pi i \mathbf{H} \cdot (\mathbf{u}_{lk} - \mathbf{u}_{l'k'})\}}. \tag{4.2.4.87}$$

In the harmonic approximation $\overline{\exp\{2\pi i \mathbf{H} \cdot \Delta\mathbf{u}\}}$ is replaced by $\exp\{\frac{1}{2}|2\pi\mathbf{H} \cdot \Delta\mathbf{u}|^2\}$. This is, however, a more or less crude approximation because strongly anharmonic vibrations are quite common in an orientationally disordered crystal. In this approximation $\overline{F_l F_{l'}^+}$ becomes

$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{-B_k(\omega_l)\}$$
$$\times \exp\{-B_{k'}(\omega_{l'})\} \exp\{D_{lk;\ l'k'}\}. \tag{4.2.4.88}$$

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