

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 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: $\omega_l = 1, \dots, D$ (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 :

$$I(\mathbf{H}, t) = \sum_l \sum_{\nu'} F_l(\mathbf{H}, t) F_{\nu'}^+(\mathbf{H}, t) \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu'})\} \quad (4.2.4.85)$$

$$F_l(\mathbf{H}, t) = \sum_k f_k \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} + \mathbf{u}_{lk})\}. \quad (4.2.4.86)$$

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.)

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

Thermal averaging gives (*cf.* Chapter 4.1)

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

In the harmonic approximation $\exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{u}\}$ 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 $F_l F_{\nu'}^+$ becomes

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

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B_k is equal to $\frac{1}{2}(2\pi\mathbf{H} \cdot \mathbf{u}_{lk})^2$ (Debye–Waller factor) and depends on the specific configuration ω_l . $D_{lk; l'k'} = \frac{(2\pi\mathbf{H} \cdot \mathbf{u}_{lk})(2\pi\mathbf{H} \cdot \mathbf{u}_{l'k'})}{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}$ includes all the correlations between positions, orientations and vibrations of the molecules.

Averaging over different configurations demands a knowledge of the orientational probabilities. The probability of finding molecule l in orientation ω_l is given by $p(\omega_l)$. The double probability $p(\omega_l, \omega_{l'})$ gives the probability of finding two molecules l, l' in different orientations ω_l and $\omega_{l'}$, respectively. In the absence of correlations between the orientations we have: $p(\omega_l, \omega_{l'}) = p(\omega_l)p(\omega_{l'})$. If correlations exist: $p(\omega_l, \omega_{l'}) = p(\omega_l)p'(\omega_l|\omega_{l'})$ where $p'(\omega_l|\omega_{l'})$ defines the conditional probability that molecule l has the orientation ω_l if molecule l' has the orientation $\omega_{l'}$. For long distances between l and l' $p'(\omega_l|\omega_{l'})$ tends to $p(\omega_{l'})$.

The difference $\Delta(\omega_l|\omega_{l'}) = p'(\omega_l|\omega_{l'}) - p(\omega_{l'})$ characterizes, therefore, the degree of short-range orientational correlation. Note that this formalism corresponds fully to the $p_{\mu}, p_{\mu\mu'}$ used in the context of translational disorder.

The average structure factor, sometimes called averaged form factor, of the molecule is given by

$$\langle F_l \rangle = \sum_{\omega_l} p(\omega_l) F_l(\omega_l). \quad (4.2.4.89)$$

(a) Negligible correlations between vibrations of different molecules (Einstein model):

$$D_{lk; l'k'} = 0 \text{ for } l \neq l'.$$

From (4.2.4.88) it follows (the prime symbol takes the Debye–Waller factor into account):

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ N \left\{ \sum_k \sum_{k'} \sum_{\omega_l} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk; l'k'}\} - |\langle F' \rangle|^2 \left. \right\} \\ &+ N \sum_{\Delta l \neq 0} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \end{aligned} \quad (4.2.4.90)$$

$L(\mathbf{H})$ is the reciprocal lattice of the well defined ordered lattice. The first term describes Bragg scattering from an averaged structure. The second term governs the diffuse scattering in the absence of short-range orientational correlations. The last term takes the correlation between the orientations into account.

If rigid molecules with centre-of-mass translational displacements and negligible librations are assumed, which is a first approximation only, $|\langle F \rangle|^2$ is no longer affected by a Debye–Waller factor.

In this approximation the diffuse scattering may therefore be separated into two parts:

$$N(\langle F^2 \rangle - |\langle F' \rangle|^2) = N(F^2 - |\langle F \rangle|^2) + N(|\langle F \rangle|^2 - |\langle F' \rangle|^2) \quad (4.2.4.91)$$

with

$$\begin{aligned} \langle F^2 \rangle &= \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} f_k(\omega_l) f_{k'}(\omega_{l'}) p(\omega_l) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}. \end{aligned} \quad (4.2.4.92)$$

The first term in (4.2.4.91) gives the scattering from equilibrium fluctuations in the scattering from individual molecules (diffuse scattering without correlations), the second gives the contribution from the centre-of-mass thermal vibrations of the molecules.

(b) If intermolecular correlations between the molecules cannot be neglected, the final intensity expression for diffuse scattering is very complicated. In many cases these correlations are caused by dynamical processes (see Chapter 4.1). A simplified treatment assumes the molecule to be a rigid body with a centre-of-mass displacement \mathbf{u}_l and neglects vibrational–librational and librational–librational correlations: $D_{l; l'} = \frac{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}$ ($l \neq l'$). The following expression approximately holds:

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ \left\langle \sum_l \sum_{l'} F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \exp\{D_{l; l'}\} \right\rangle \{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \\ &+ N \left\{ \sum_{\omega_l} \sum_{k, k'} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk; l'k'}\} - \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} p(\omega_l) p(\omega_{l'}) f_k f_{k'} \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \\ &\times \exp\{D_{lk; l'k'}\} \left. \right\} + \sum_{l \neq l'} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \exp\{D_{l; l'}\}. \end{aligned} \quad (4.2.4.93)$$

Again the first term describes Bragg scattering and the second corresponds to the average thermal diffuse scattering in the disordered crystal. Because just one molecule belongs to one unit cell only acoustic waves contribute to this part. To an approximation, the result for an ordered crystal may be used by replacing F by $\langle F' \rangle$ [Chapter 4.1, equation (4.1.3.4)]. The third term corresponds to random-disorder diffuse scattering. If librations are neglected this term may be replaced by $N(\langle F^2 \rangle - \langle F \rangle^2)$. The last term in (4.2.4.93) describes space correlations. Omission of $\exp\{D_{l; l'}\}$ or expansion to $\sim (1 + D_{l; l'})$ are further simplifying approximations.

In either (4.2.4.90) or (4.2.4.93) the diffuse-scattering part depends on a knowledge of the conditional probability $\Delta(\omega_l|\omega_{l'})$ and the orientational probability $p(\omega_l)$. The latter may be found, at least in principle, from the average structure factor.

4.2.4.5.2. Rotational structure (form) factor

In certain cases and with simplifying assumptions, $\langle F \rangle$ [equation (4.2.4.89)] and $\langle \Delta F^2 \rangle$ [equation (4.2.4.92)] may be calculated. Assuming only one molecule per unit cell and treating the molecule as a rigid body, one derives from the structure factor of an ordered crystal F_l

$$\langle F \rangle = \sum_k f_k \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \quad (4.2.4.94)$$

and

$$\begin{aligned} \langle \Delta F^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} [\langle \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \rangle \\ &- \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{l'k'}\} \rangle]. \end{aligned} \quad (4.2.4.95)$$

If the molecules have random orientation in space the following expressions hold [see, *e.g.*, Dolling *et al.* (1979)]:

$$\langle F \rangle = \sum_k f_k j_0(\mathbf{H} \cdot \mathbf{r}_k) \quad (4.2.4.96)$$

$$\begin{aligned} \langle |\Delta F|^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} \{ j_0(\mathbf{H} \cdot (\mathbf{r}_k - \mathbf{r}_{k'})) \\ &- j_0(\mathbf{H} \cdot \mathbf{r}_k) j_0(\mathbf{H} \cdot \mathbf{r}_{k'}) \}. \end{aligned} \quad (4.2.4.97)$$

$j_0(z)$ is the zeroth order of the spherical Bessel functions and describes an atom k uniformly distributed over a shell of radius r_k .