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:

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

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.)

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

Thermal averaging gives (*cf.* Chapter 4.1)

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

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

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

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

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B_k is equal to $\frac{1}{2}\overline{(2\pi\mathbf{H}\cdot\mathbf{u}_{lk})^2}$ (Debye–Waller factor) and depends on the specific configuration ω_l. $D_{lk;\,l'k'} = \overline{(2\pi\mathbf{H}\cdot\mathbf{u}_{lk})(2\pi\mathbf{H}\cdot\mathbf{u}_{l'k'})}$ 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_μ, $p_{\mu\mu'}$ used in the context of translational disorder.

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

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

(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):

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

$L(\mathbf{H})$ 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:

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

with

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

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: $D_{l;\,l'} = \overline{(2\pi\mathbf{H}\cdot\mathbf{u}_l)(2\pi\mathbf{H}\cdot\mathbf{u}_{l'})}$ ($l \neq l'$). The following expression approximately holds:

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

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

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

and

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

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

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

$$\langle |\Delta F|^2 \rangle = \sum_k \sum_{k'} f_k f_{k'}\{ j_0[\mathbf{H}\cdot(\mathbf{r}_k - \mathbf{r}_{k'})]$$
$$- j_0(\mathbf{H}\cdot\mathbf{r}_k) j_0(\mathbf{H}\cdot\mathbf{r}_{k'})\}. \qquad (4.2.4.97)$$

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

In practice the molecules perform more or less finite librations about the main orientation. The structure factor may then be found by the method of symmetry-adapted functions [see, *e.g.*, Press (1973), Press & Hüller (1973), Dolling *et al.* (1979), Prandl (1981, and references therein)].

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_{\mu=-\nu}^{+\nu} i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{(k)} Y_{\nu\mu}(\theta, \varphi). \qquad (4.2.4.98)$$

$j_\nu(z)$ is the νth order of spherical Bessel functions, the coefficients $C_{\nu\mu}^{(k)}$ characterize the angular distribution of $\mathbf{r}_k$, $Y(\theta, \varphi)$ are the spherical harmonics where $|\mathbf{H}|, \theta, \varphi$ denote polar coordinates of $\mathbf{H}$.

The general case of an arbitrary crystal, site and molecular symmetry and the case of several symmetrically equivalent orientationally disordered molecules per unit cell are treated by Prandl (1981); an example is given by Hohlwein *et al.* (1986). As mentioned above, cubic plastic crystals are common and therefore mostly studied up to now. The expression for $\langle F \rangle$ may then be formulated as an expansion in cubic harmonics, $K_{\nu\mu}(\theta, \varphi)$:

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_\mu i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{\prime(k)} K_{\nu\mu}(\theta, \varphi). \qquad (4.2.4.99)$$

($C_{\nu\mu}'$ are modified expansion coefficients.)

Taking into account isotropic centre-of-mass translational displacements, which are not correlated with the librations, we obtain:

$$\langle F' \rangle = \langle F \rangle \exp\{-\tfrac{1}{6}H^2 \langle U^2 \rangle\}. \qquad (4.2.4.100)$$

U is the mean-square translational displacement of the molecule. Correlations between translational and vibrational displacements are treated by Press *et al.* (1979).

Equivalent expressions for crystals with symmetry other than cubic may be found from the same concept of symmetry-adapted functions [tables are given by Bradley & Cracknell (1972)].

4.2.4.5.3. *Short-range correlations*

The final terms in equations (4.2.4.90) and (4.2.4.93) concern correlations between the orientations of different molecules. Detailed evaluations need a knowledge of a particular model. Examples are compounds with nitrate groups (Wong *et al.*, 1984; Lefebvre *et al.*, 1984), CBr$_4$ (More *et al.*, 1980, 1984), and many others (see Sherwood, 1979). The situation is even more complicated when a modulation wave with respect to the occupation of different molecular orientations is superimposed. A limiting case would be a box-like function describing a pattern of domains. Within one domain all molecules have the same orientation. This situation is common in ferroelectrics where molecules exhibit a permanent dipole moment. The modulation may occur in one or more directions in space. The observed intensity in this type of orientationally disordered crystal is characterized by a system of more or less diffuse satellite reflections. The general scattering theory of a crystal with occupational modulation waves follows the same lines as outlined in Section 4.2.3.1.

4.2.5. Measurement of diffuse scattering

To conclude this chapter experimental aspects are summarized which are specifically important in diffuse-scattering work. The summary is restricted to film methods commonly used in laboratories and (X-ray or neutron) diffractometer measurements. Sophisticated special techniques and instruments at synchrotron facilities and reactors dedicated to diffuse-scattering work are not described here. The full merit of these machines may be assessed after inspection of corresponding user handbooks which are available upon request. Also excluded from this section are instruments and methods related to diffuse scattering at low angles, *i.e.* small-angle scattering techniques. Although no fundamental differences exist between an X-ray experiment in a laboratory and at a synchrotron facility, some specific points have to be considered in the latter case. These are discussed by Matsubara & Georgopoulos (1985), Oshima & Harada (1986), and Ohshima *et al.* (1986).

Generally, diffuse scattering is weak in comparison with Bragg scattering, anisotropically and inhomogeneously distributed in reciprocal space, elastic, inelastic, or quasi-elastic in origin. It is frequently related to more than one structural element, which means that different parts may show different behaviour in reciprocal space and/or on an energy scale. Therefore special care has to be taken concerning the following points: (1) type of experiment: X-rays or neutrons, film or diffractometer/spectrometer, single crystal or powder; (2) strong sources; (3) best choice of wavelength (or energy) of incident radiation if no 'white' technique is used; (4) monochromatic and focusing techniques; (5) sample environment and background reduction; (6) resolution and scanning procedure in diffractometer or densitometer recording.

On undertaking an investigation of a disorder problem by an analysis of the diffuse scattering an overall picture should first be recorded by X-ray diffraction experiments. Several sections through reciprocal space help to define the problem. For this purpose film methods are preferable. Cameras with relatively short crystal–film distances avoid long exposure times. Unfortunately, there are some disorder problems which cannot be tackled by X-ray methods. X-rays are rather insensitive for the elucidation of disorder problems where light atoms in the presence of heavy atoms play the dominant role, or when elements are involved which scarcely differ in X-ray scattering amplitudes (*e.g.* Al/Si/Mg). In these cases neutrons have to be used at an early stage. If a significant part of the diffuse scattering is suspected not to be of static origin concomitant purely elastic, quasi-elastic or inelastic neutron experiments have to be planned from the very beginning.

Because diffuse scattering is usually weak, intense radiation sources are needed, whereas the background level should be kept as low as possible. Coming to the background problem later, we should make some brief remarks concerning sources. Even a normal modern X-ray tube is a stronger source, defined by the flux density from an anode (number of photons cm^{-2} s^{-1}), than a reactor with the highest available flux. For this reason most experimental work which can be performed with X-rays should be. Generally the characteristic spectrum will be used, but special methods have been developed where the white X-ray spectrum is of interest (see below). A most powerful source in this respect is a modern synchrotron storage ring (see, *e.g.*, Kunz, 1979). With respect to rotating anodes one should bear in mind not only the power but also the flux density, because there is little merit for a broad focus in diffuse-scattering work (separation of sharp and diffuse scattering). One can suppose that synchrotron radiation in the X-ray range will also play an important role in the field of monochromatic diffraction methods, owing to the extremely high brilliance of these sources (number of quanta cm^{-2}, sr^{-1}, s^{-1} and wavelength interval). Diffuse neutron-diffraction work may only be performed on a high- or medium-flux reactor. Highly efficient monochromator systems are necessary. In combination with time-of-flight neutron methods pulsed sources are nowadays equivalent to reactors (Windsor, 1982).

If film and (X-ray) diffractometer methods are compared, film techniques are highly recommended at an early stage to give a general survey of the disorder problem. Routine X-ray techniques such as rotation photographs, Weissenberg or precession techniques may be used. The Weissenberg method is preferred to the