4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

Georgopoulos & Cohen, 1977; Wu *et al.*, 1983). The method does not work for neutron diffraction. Also, the case of planar short-range order with corresponding diffuse intensity along rods in reciprocal space may be treated along the Borie & Sparks method (Ohshima & Moss, 1983).

Multi-wavelength methods taking advantage of the variation of the structure factor near an absorption edge (anomalous dispersion) are discussed by Cenedese *et al.* (1984). The same authors show that in some cases the neutron method allows for a contrast variation by using samples with different isotope substitution.

4.2.4.4.6. *Powder diffraction*

Evaluation of diffuse-scattering data from powder diffraction follows the same theoretical formulae developed for the determination of the radial distribution function for glasses and liquids (Debye & Menke, 1931; Warren & Gingrich, 1934). The final formula for random distributions may be given as (Fender, 1973)

$$I_d^p = \{\langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2\} \sum_i s_i \sin(2\pi H r_i)/(2\pi H r_i).$$

$$(4.2.4.82)$$

s_i represents the number of atoms at distance r_i from the origin. An equivalent expression for a substitutional binary alloy is

$$I_d^p = \alpha(1-\alpha)\{|f_2(\mathbf{H}) - f_2(\mathbf{H})|^2\} \sum_i s_i \sin(2\pi H r_i)/(2\pi H r_i).$$

$$(4.2.4.83)$$

4.2.4.4.7. *Small concentrations of defects*

In the literature small concentrations are treated in terms of fluctuations of the functions $\pi_{\mathbf{n}\nu}$ as defined in equation (4.2.4.56). Generally we prefer the introduction of the distribution function of the defects or clusters. Since this problem has already been treated in Section 4.2.4.4.3 only some very brief remarks are given here. The most convenient way to derive the distribution function correctly from experimental data is the use of low-angle scattering which generally shows one or more clear maxima caused by partly periodic properties of the distribution function. For the deconvolution of the distribution function, received by Fourier transformation of the corrected diffused low-angle scattering, the reader is referred to the relevant literature. Since deconvolutions are not unique some reasonable assumptions are necessary for the final solution. Anomalous scattering may be very helpful if applicable.

4.2.4.4.8. *Cluster method*

As mentioned above, the cluster method may be useful for the interpretation of disorder problems. In the general formula of diffuse scattering of random distributions equation (4.2.2.13) may be used. Here $|\langle F(\mathbf{H}) \rangle|^2$ describes the sharp Bragg maxima, while $|\Delta F(\mathbf{H})|^2 = \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2$ represents the contribution to diffuse scattering. Correlation effects can also be taken into account by using clusters of sufficient size if their distribution may be considered as random in good approximation. The diffuse intensity is then given by

$$I_d(\mathbf{H}) = \sum_\nu p_\nu |F_\nu(\mathbf{H})|^2 - |\sum_\nu p_\nu F_\nu(\mathbf{H})|^2, \qquad (4.2.4.84)$$

where $F_\nu(\mathbf{H})$ represents the difference structure factor of the νth cluster and p_ν is its *a priori* probability. Obviously equation (4.2.4.84) is of some use in two cases only. (1) The number of clusters is sufficiently small and meets the condition of nearly random distribution. In principle, its structure may then be determined with the aid of refinement methods according to

equation (4.2.4.84). Since the second term is assumed to be known from the average structure, the first term may be evaluated by introducing as many parameters as there are clusters involved. A special computer program for incoherent refinement has to be used if more than one representative cluster has to be introduced. In the case of more clusters, constraints are necessary. (2) The number of clusters with similar structures is not limited. It may be assumed that their size distribution may be expressed by well known analytical expressions, *e.g.* Gaussians or Lorentzians. The distribution is still assumed to be random.

An early application of the cluster method was the calculation of the diffuse intensity of Guinier–Preston zones, where a single cluster is sufficient (see, *e.g.*, Gerold, 1954; Bubeck & Gerold, 1984). Unfortunately no refinements of cluster structures have so far been published. The full theory of the cluster method was outlined by Jagodzinski & Haefner (1967).

Some remarks on the use of residual factors should be added here. Obviously the diffuse scattering may be used for refinements in a similar way as in conventional structure determination. For this purpose a sufficiently small reciprocal lattice has to be defined. The size of the reciprocal cell has to be chosen with respect to the maximum gradient of diffuse scattering. Then the diffuse intensity may be described by a product of the real intensity distribution and the small reciprocal lattice. Fourier transformation yields the convolution of the real disordered structure and a large unit cell. In other words, the disordered structure is subdivided into large units and subsequently superimposed ('projected') in a single cell. In cases where a clear model of the disorder could be determined, a refinement procedure for atomic and other relevant parameters can be started. In this way a residual factor may be determined. A first approach has been elaborated by Epstein & Welberry (1983) in the case of substitutional disorder of two molecules.

The outstanding limiting factor is the collection of weak intensity data. The amount increases rapidly with the complexity of the structure and could even exceed by far the amount which is needed in the case of protein structure refinement. Hence, it seems to be reasonable to restrict the measurement to distinct areas in reciprocal space. Most of these publications, however, use too little information when compared with the minimum of data which would be necessary for the confirmation of the proposed model. Hence, physical and chemical considerations should be used as an additional source of information.

4.2.4.4.9. *Comparison between X-ray and neutron methods*

Apart from experimental arguments in favour of either method, there are some specific points which should be mentioned in this context. The diffuse scattering in question must be separated from Bragg scattering and from other diffuse-scattering contributions. Generally both methods are complementary: neutrons are preferable in cases where X-rays show only a small scattering contrast: (heavy) metal hydrides, oxides, carbides, Al–Mg distribution *etc*. In favourable cases it is possible to suppress (nuclear) Bragg scattering of neutrons when isotopes are used so that $\sum_\nu c_\nu f_\nu = 0$ for all equivalent positions. Another way to separate Bragg peaks is to record the diffuse intensity, if possible, at low $|\mathbf{H}|$ values. This can be achieved either by measurement at low θ angles or by using long wavelengths. For reasons of absorption the latter point is the domain of neutron scattering. Exceeding the Bragg cut-off, Bragg scattering is ruled out. In this way 'diffuse' background owing to multiple Bragg scattering is avoided. Other diffuse-scattering contributions which increase with the $|\mathbf{H}|$ value are thus also minimized: thermal diffuse scattering (TDS) and scattering due to long-range static displacements. On the other hand, lattice distortions, Huang scattering, . . . should be measured at large values of $|\mathbf{H}|$. TDS

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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:

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

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.)

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

Thermal averaging gives (*cf.* Chapter 4.1)

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

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

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