

## 4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

developed approaches using computer simulations are described in Section 4.2.7.

Here we give only some general remarks on order–disorder problems.

Correlation functions in three dimensions may have very complicated periodicities; hence careful study is necessary to establish whether or not they may be interpreted in terms of a superlattice. If so, extinction rules have to be determined in order to obtain information on the superspace group. In the literature these are often called modulated structures (see Section 4.2.6) because a sublattice, as determined by the basic lattice, and a superlattice may well be defined in reciprocal space: reflections of a sublattice including (000) are formally described by a multiplication by a lattice having larger lattice constants (the superlattice) in reciprocal space; in real space this means a convolution with the Fourier transform of this lattice (the sublattice). In this way, the averaged structure is generated in each of the subcells (the superposition or ‘projection’ of all subcells into a single one). Obviously, the Patterson function of the averaged structure contains little information in the case of small subcells. Hence it is advisable to include the diffuse scattering of the superlattice reflections at the beginning of any structure determination.

$N$  subcells in real space are assumed, each of them representing a kind of a complicated ‘atom’ that may be equal by translation or other symmetry operation. Once a superspace group has been determined, the usual extinction rules of space groups may be applied, remembering that the ‘atoms’ themselves may have systematic extinctions. Major difficulties arise from the existence of different symmetries of the subgroup and the supergroup. Since the symmetry of the supercell is lower in general, all missing symmetry elements may cause domains corresponding to the missing symmetry element: translations cause antiphase domains in their generalized sense; other symmetry elements cause twins generated by rotations, mirror planes or the centre of symmetry. If all these domains are small enough to be detected by a careful study of line profiles, using diffraction methods with a high resolution power, the structural study may be facilitated by introducing scaling factors for groups of reflections affected by the possible domain structures.

## 4.2.3.6. Symmetry

If disorder problems involving completely different structures (exsolutions *etc.*) are excluded, in general the symmetry of the diffuse-scattering pattern is the same as that of the Bragg peaks, *i.e.* it corresponds to the point group of the space group of the average structure. Only under specific directional growth conditions are deviations from this rule conceivable (although seemingly not very common). On the other hand, the symmetry of the underlying disorder model in direct space may be lower than that of the space group of the average structure (it is usually a subgroup of the space group of the average structure). The overall symmetry in reciprocal space is then restored by employing the missing (point-group) symmetry elements, which have therefore to be used in the calculation of the full diffraction pattern.

From these arguments, some specific disorder models may be classified according to the irreducible representations of the space group of the average structure. While for general wavevectors in the Brillouin zone no further restrictions appear, for high-symmetry directions consideration of the irreducible representations of the little co-group of the wavevector can help to identify the different symmetries of the disorder model. This becomes particularly evident when the modulation-wave approach is used as shown *e.g.* by Welberry & Withers (1990) and Welberry & Butler (1994). Of particular value are observed extinction rules, which may be calculated by group-theoretical methods as developed by Perez-Mato *et al.* (1998) for the extinctions occurring in inelastic neutron-scattering experiments.

In favourable cases, the analysis of such extinctions alone can lead to a unique determination of the disorder model (see, *e.g.*, Aroyo *et al.*, 2002).

## 4.2.4. General guidelines for analysing a disorder problem

In general, the structure determination of a disordered crystal should start in the usual way by solving the average structure. The effectiveness of this procedure strongly depends on the distribution of integrated intensities of sharp and diffuse reflections. In cases where the integrated intensities of Bragg peaks are predominant, the maximum information can be drawn from the averaged structure. The observations of fractional occupations of lattice sites, split positions and anomalous large and anharmonic displacement parameters are indications of the disorder involved. Since these aspects of disorder phenomena in the averaged structure may be interpreted very easily, a detailed discussion of this matter is not given here (see any modern textbook of X-ray crystallography). Therefore, the anomalies of the average structure can give valuable hints on the underlying disorder and, *vice versa*, can be used to check the final disorder model derived from the diffuse scattering.

Difficulties may arise from the intensity integration, which should be carried out very carefully to separate the Bragg peaks from the diffuse contributions, *e.g.* by using a high-resolution diffraction method. The importance of this may be understood from the following argument. The averaged structure is determined by the coherent superposition of different structure factors. This interpretation is true if there is a strictly periodic subcell with long-range order that allows for a clear separation of sharp and diffuse scattering. There are important cases, however, where this procedure cannot be applied without loss of information.

(a) The diffuse scattering (other than thermal diffuse scattering) is concentrated near the Bragg peaks for a large number of reflections. Because of the limited resolution power of conventional single-crystal methods, the separation of sharp and diffuse scattering is impossible. Hence, the conventional study of integrated intensities does not really lead to an averaged structure. In this case, a refinement should be tried using an incoherent superposition of different structure factors (from the average structure and the difference structure). Application of this procedure is subject to conditions which have to be checked very carefully before starting the refinement: first, it is necessary to estimate the amount of diffuse scattering not covered by intensity integration of the ‘sharp’ reflections. Since loss in intensity, hidden in the background scattering, is underestimated very frequently, it should be checked whether nearly coinciding sharp and diffuse maxima are modulated by the same structure factor. It may be difficult to meet this condition in some cases; *e.g.* this condition is fulfilled for antiphase domains but the same is not true for twin domains.

(b) The concentration of diffuse maxima near Bragg peaks is normally restricted to domain structures with a strictly periodic sublattice. Cases deviating from this rule are possible. Since they are rare, they are omitted here. Even structures with small deviations from the average structure do not necessarily lead to structure factors for diffuse scattering that are proportional to those of the average structure. This has been shown in the case of a twin structure correlated by a mirror plane, where the reflections of a zone only have equal structure factors (Cowley & Au, 1978). This effect causes even more difficulties for orthogonal lattices, where the two twins have reflections in exactly the same positions, although differing in their structure factors. In this particular case, the incoherent or coherent treatment in refinements may be seriously hampered by strains originating from the boundary. Unsatisfactory refinements may be explained in this way but this does not improve their reliability.

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

The integrated intensity within a Brillouin zone of any structure is independent of atomic positions if the atomic form factors remain unchanged by structural fluctuations. Small deviations of atomic form factors owing to electron-density changes of valence electrons are neglected. Consequently, the integrated diffuse intensities remain unchanged if the average structure is not altered by the degree of order. The latter condition is obeyed in cases where a geometrical long-range order of the lattice is independent of the degree of order, and no long-range order in the structure exists. This law is extremely useful for the interpretation of diffuse scattering. Unfortunately, intensity integration over coinciding sharp and diffuse maxima does not necessarily lead to a structure determination of the corresponding undistorted structure. This integration may be useful for antiphase domains without major structural changes at the boundaries. In all other cases, the deviations of domains (or clusters) from the averaged structure determine the intensities of maxima, which are no longer correlated with those of the average structure.

If the integrated intensity of diffuse scattering is comparable with, or even larger than, those of the Bragg peaks, it is useful to begin the interpretation with a careful statistical study of the diffuse intensities. Intensity statistics can be applied in a way similar to the intensity statistics in classical structure determination. The following rules are briefly discussed in order to enable a semiquantitative interpretation of the essential features of disorder.

(1) First, it is recommended that the integrated intensities are studied in certain areas of reciprocal space.

(2) Since low-angle scattering is very sensitive to fluctuations of densities, the most important information can be drawn from its intensity behaviour. If there is at least a one-dimensional sublattice in reciprocal space without diffuse scattering, it may often be concluded that there is no important low-angle scattering either. This law is subject to the condition of a sufficient number of reflections obeying this extinction rule without any exception.

(3) If the diffuse scattering shows maxima and minima, it should be checked whether the maxima observed may be approximately assigned to a lattice in reciprocal space. Obviously, this condition can hardly be met exactly if these maxima are modulated by a kind of structure factor, which causes displacements of maxima proportional to the gradient of this structure factor. Hence this influence may well be estimated from a careful study of the complete diffuse diffraction pattern.

It should then be checked whether the corresponding lattice represents a sub- or superlattice of the structure. An increase of the width of reflections as a function of increasing  $|\mathbf{H}|$  indicates strained clusters of this sub- or superlattice.

(4) The next step is to search for extinction rules for the diffuse scattering. The simplest is the lack of low-angle scattering, which has already been mentioned above. Since diffuse scattering is generally given by equation (4.2.3.23b),

$$I_D(\mathbf{H}) = \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \\ = \sum_{\mu} p_{\mu} |F_{\mu}(\mathbf{H})|^2 - \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2,$$

it may be concluded that this condition is fulfilled in cases where all structural elements participating in disorder differ by translations only (stacking faults, antiphase domains *etc.*). They add phase factors to the various structure factors, which may become  $n2\pi$  ( $n = \text{integer}$ ) for specific values of the reciprocal vector  $\mathbf{H}$ . If all  $p_{\mu}$  are equivalent by symmetry

$$p \sum_{\mu} |F_{\mu}(\mathbf{H})|^2 - \left[ p \sum_{\mu} F_{\mu}(\mathbf{H}) \right] \left[ p \sum_{\mu} F_{\mu}^+(\mathbf{H}) \right] = 0.$$

Other possibilities for vanishing diffuse scattering may be derived in a similar manner for special reflections if glide operations are responsible for disorder. Since we are concerned with disordered structures, these glide operations need not necessarily be a symmetry operation of the lattice. It should be pointed out, however, that all these extinction rules of diffuse scattering are a kind of 'anti'-extinction rule, because they are valid for reflections having maximum intensity for the sharp reflections unless the structure factor itself vanishes.

(5) Furthermore, it is important to plot the integrated intensities of sharp and diffuse scattering as a function of the reciprocal coordinates, at least in a semiquantitative way. If the ratio of integrated intensities remains constant in the statistical sense, we are predominantly concerned with a density phenomenon. It should be pointed out, however, that a particle-size effect of domains behaves like a density phenomenon (the density changes at the boundary!).

If the ratio of 'diffuse' to 'sharp' intensities increases with diffraction angle, we have to take into account atomic displacements. A careful study of this ratio yields very important information on the number of displaced atoms. The result has to be discussed separately for domain structures if the displacements are equal in the subcells of a single domain but different for the various domains. In the case of two domains with displacements of all atoms, the integrated intensities of sharp and diffuse reflections become statistically equal for large  $|\mathbf{H}|$ . Other rules may be derived from statistical considerations.

(6) The next step of a semiquantitative interpretation is to check the intensity distribution of diffuse reflections in reciprocal space. In general this modulation is simpler than that of the sharp reflections. Hence it is frequently possible to start a structure determination with diffuse scattering. This method is extremely helpful for one- and two-dimensional disorder where partial structure determinations yield valuable information, even for the evaluation of the average structure.

(7) In cases where no sub- or superlattice belonging to the diffuse scattering can be determined, a careful check of integrated intensities in the neighbourhood of Bragg peaks should again be performed. If systematic absences are found, the disorder is most probably restricted to specific lattice sites which may also be found in the average structure. The accuracy, however, is much lower here. If no such effects correlated with the average structure are observed, the disorder problem is related to a distribution of molecules or clusters with a structure differing from the average structure. As pointed out in Section 4.2.3.1, the problem of the representative structure(s) of the molecule(s) or the cluster(s) should be solved. Furthermore, their distribution function(s) is (are) needed. In this particular case, it is very useful to start with a study of diffuse intensity at low diffraction angles in order to acquire information about density effects. Despite the contribution to sharp reflections, one should remember that the level of information derived from the average structure may be very low (*e.g.* small displacements, low concentrations *etc.*).

(8) A Patterson picture – or strictly speaking a difference Patterson ( $|\Delta F|^2$  Fourier synthesis) – may be very useful in this case. This method is promising in the case of disorder in molecular structures where the molecules concerned are at least partly known. Hence the interpretation of the difference Patterson may start with some internal molecular distances. Nonmolecular structures show some distances of the average structure. Consequently, a study of the important distances will yield information on displacements or replacements in the average structure. For a detailed study of this matter the reader is referred to the literature (Schwartz & Cohen, 1977).

Although it is highly improbable that exactly the same diffraction picture will be found, the use of an atlas of optical transforms (Wooster, 1962; Harburn *et al.*, 1975; Welberry & Withers, 1987) may be helpful at the beginning of any study of

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diffuse scattering. Alternatively, computer simulations may be helpful, as discussed in Section 4.2.7. The most important step is the separation of the distribution function from the molecular scattering. Since this information may be derived from a careful comparison of low-angle diffraction with the remaining sharp reflections, this task is not too difficult. If the influence of the distribution function is unknown, the reader is strongly advised to disregard the immediate neighbourhood of Bragg peaks in the first step of the interpretation. Obviously information may be lost in this way but, as has been shown in the past, much confusion caused by an attempt to interpret the scattering near the Bragg peaks with specific structural properties of a cluster or molecular model is avoided. The inclusion of this part of diffuse scattering can be made after a complete interpretation of the change of the influence of the distribution function on diffraction in the wide-angle region.

### 4.2.5. Quantitative interpretation

#### 4.2.5.1. Introduction

In these sections, quantitative interpretations of the elastic part of X-ray and neutron diffuse scattering are outlined. Although similar relations are valid for the magnetic scattering of neutrons, this particular topic is excluded. Obviously, all disorder phenomena are strongly temperature-dependent if thermal equilibrium is reached. Consequently, the interpretation of diffuse scattering should include a statistical thermodynamical treatment. Unfortunately, no quantitative theory for the interpretation of structural phenomena is so far available: all quantitative solutions introduce formal order parameters such as correlation functions or distributions of defects. At low temperatures (*i.e.* with a low concentration of defects) the distribution function plays the dominant role in diffuse scattering. With increasing temperature the number of defects increases with corresponding strong interactions between them. Therefore, correlations become increasingly important, and phase transformations of first or higher order may occur which need a separate theoretical treatment. In many cases, large fluctuations of structural properties occur that are closely related to the dynamical properties of the crystal. Theoretical approximations are possible, but their presentation is far beyond the scope of this article. Hence we restrict ourselves to formal parameters in the following.

Point defects or limited structural units, such as molecules, clusters of finite size *etc.*, may only be observed in diffraction if there is a sufficiently large number of defects. This statement is no longer true in high-resolution electron diffraction, where single defects may be observed either by diffraction or by optical imaging if their contrast is high enough. Hence electron microscopy and diffraction are valuable methods in the interpretation of disorder phenomena.

The arrangement of a finite assembly of structural defects is described by its structure and its three-dimensional (3D) distribution function. Structures with a strict 1D periodicity (chain-like structures) need a 2D distribution function, while for structures with a 2D periodicity (layers) a 1D distribution function is sufficient. Since the distribution function is the dominant factor in statistics with correlations between defects, we define the dimensionality of disorder as that of the corresponding distribution function. This definition is more effective in diffraction problems because the dimension of the disorder problem determines the dimension of the diffuse scattering: 1D diffuse streaks, 2D diffuse layers or a general 3D diffuse scattering.

Strictly speaking, completely random distributions cannot be realized, as shown in Section 4.2.3. They occur approximately if the following conditions are satisfied:

(1) The average volume of all defects including their surrounding strain fields  $NcV_d$  (where  $N$  is the number of unit

cells,  $c$  is the concentration of defects and  $V_d$  is the volume of the defect with  $V_d > V_c$ ,  $V_c$  being the volume of the unit cell) is small in comparison with the total volume  $NV_c$  of the crystal, or  $V_c \gg cV_d$ .

(2) Interactions between the defects are negligible. These conditions, however, are valid in very rare cases only, *i.e.* where small concentrations and vanishing strain fields are present. Remarkable exceptions from this rule are real point defects without interactions, such as isotope distribution (which can be studied by neutron diffraction) or the system AuAg at high temperature.

As already mentioned, disorder phenomena may be observed in thermal equilibrium. Two completely different cases have to be considered:

(1) The concentration of defects is given by the chemical composition, *i.e.* impurities in a closed system.

(2) The number of defects increases with temperature and also depends on pressure or other parameters, *i.e.* interstitials, voids, static displacements of atoms, stacking faults, dislocations *etc.*

In many cases, the defects do not occur in thermal equilibrium. Nevertheless, their diffuse scattering is temperature-dependent because of the anomalous thermal movements at the boundary of the defect. Hence the observation of a temperature-dependent behaviour of diffuse scattering cannot be taken as a definite criterion of thermal equilibrium without further careful interpretation.

Ordering of defects may take place in a very anisotropic manner. This is demonstrated by the huge number of examples of 1D disorder. As shown by Jagodzinski (1963), this type of disorder cannot occur in thermal equilibrium for the infinite crystal. This type of disorder is generally formed during crystal growth or mechanical deformation. Similar arguments may be applied to 2D disorder. This is a further reason why the Ising model can hardly ever be used to obtain interaction energies of structural defects. From these remarks it becomes clear that order parameters are formal parameters without strict thermodynamical meaning.

The following section is organized as follows: first we discuss the simple case of 1D disorder where reliable solutions of the diffraction problem are available. Intensity calculations for diffuse scattering from 2D disorder by chain-like structures follow. Finally, the 3D case is treated, where formal solutions of the diffraction problem have been tried and applied successfully to metallic systems to some extent. A short concluding section concerns the special phenomenon of orientational disorder.

#### 4.2.5.2. Layered structures: one-dimensional disorder

As has been pointed out above, it is often useful to start the interpretation of diffuse scattering by checking the diffraction pattern with respect to the dimensionality of the disorder concerned. Since each disordered direction in the crystal demands a violation of the corresponding Laue condition, this question may easily be answered by looking at the diffuse scattering. Diffuse streaks in reciprocal space are due to a one-dimensional violation of the Laue conditions, and will be called one-dimensional disorder. This kind of order is typical for layer structures, but it is frequently observed in cases where several sequences of layers do not differ in the interactions of next-nearest neighbours. Typical examples are structures which may be described in terms of close packing, *e.g.* hexagonal and cubic close packing.

For a quantitative interpretation of diffuse streaks we need one-dimensional correlation functions, which may be determined uniquely if a single independent correlation function is active. According to equation (4.2.3.50), Fourier transformation yields the information required. In all other cases, a specific model has to be suggested for a full interpretation of diffuse streaks. It is worth noting that disorder parameters can be defined uniquely