4. DIFFUSE SCATTERING AND RELATED TOPICS

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 a reasonable explanation of scaling factors to be introduced for groups of reflections affected by the possible domain structures.

(9) *Density modulations*

A density modulation of a structure in real space leads to pairs of satellites in reciprocal space. Each main reflection is accompanied by a pair of satellites in the directions $\mp \Delta\mathbf{H}$ with phases $\mp 2\pi\varphi$. The reciprocal lattice may then be written in the following form ($0 \le \alpha \le 1$):

$$L(\mathbf{H}) + \frac{\alpha}{2} L(\mathbf{H} + \Delta\mathbf{H}) \exp\{2\pi i \Phi\}$$
$$+ \frac{\alpha}{2} L(\mathbf{H} - \Delta\mathbf{H}) \exp\{2\pi i (-\Phi)\}.$$

Fourier transformation yields

$$l(\mathbf{r}) \left[1 + \frac{\alpha}{2} \exp\{2\pi i (\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} \right.$$
$$\left. + \frac{\alpha}{2} \exp\{-2\pi i (\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} \right]$$
$$= l(\mathbf{r})[1 + \alpha \cos(2\pi\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)]. \qquad (4.2.3.34)$$

Equation (4.2.3.34) describes the lattice modulated by a harmonic density wave. Since phases cannot be determined by intensity measurements, there is no possibility of obtaining any information on the phase relative to the sublattice. From (4.2.3.34) it is obvious that the use of higher orders of harmonics does not change the situation. If $\Delta\mathbf{H}$ is not rational such that $n\Delta\mathbf{H}$ ($n =$ integer) does not coincide with a main reflection in reciprocal space, the modulated structure is incommensurate with the basic lattice, and the phase of the density wave becomes meaningless. The same is true for the relative phases of the various orders of harmonic modulations of the density. This uncertainty even remains valid for commensurate density modulations of the sublattice, because coinciding higher-order harmonics in reciprocal space cause the same difficulty; higher-order coefficients cannot uniquely be separated from lower ones, consequently structure determination becomes impossible unless phase-determination methods are applied. Fortunately, density modulations of pure harmonic character are impossible for chemical reasons; they may be approximated by disorder phenomena for the averaged structure only. If diffuse scattering is taken into account the situation is changed considerably: A careful study of the diffuse scattering alone, although difficult in principle, will yield the necessary information about the relative phases of density waves (Korekawa, 1967).

(10) *Displacement modulations*

Displacement modulations are more complicated, even in a primitive structure. The Fourier transform of a longitudinal or a transverse displacement wave has to be calculated and this procedure does not result in a function of similar simplicity. A set of satellites is generated whose amplitudes are described by Bessel functions of νth order, where ν represents the order of the satellites. With α as amplitude of the displacement wave the intensity of the satellites increases with the magnitude of the product $H\alpha$. This means that a single harmonic displacement causes an infinite number of satellites. They may be unobservable at low diffraction angles as long as the amplitudes are small. If the displacement

modulation is incommensurate there are no coincidences with reflections of the sublattice. Consequently, the reciprocal space is completely covered with an infinite number of satellites, or, in other words, with diffuse scattering. This is a clear indication that incommensurate displacement modulations belong to the category of disordered structures. Statistical fluctuations of amplitudes of the displacement waves cause additional diffuse scattering, regardless of whether the period is commensurate or incommensurate (Overhauser, 1971; Axe, 1980). Fluctuations of 'phases' (= periods) cause a broadening of satellites in reciprocal space, but no change of their integrated intensities as long as the changes are not correlated with fluctuation periods. The broadening of satellite reflections increases with the order of satellites and ($\mathbf{H} \cdot \mathbf{a}$). Obviously, there is no fundamental difference in the calculation of diffuse scattering with an ordered supercell of sufficient size.

The use of optical transforms has been revived recently, although its efficiency is strongly dependent on the availability of a useful computer program capable of producing masks for optical diffraction. An atlas of optical transforms is available (Wooster, 1962; Harburn *et al.*, 1975), but the possibility cannot be excluded that the diffuse scattering observed does not fit well into one of the diffraction pictures shown. Yet one of the major advantages of this optical method is the simple experimental setup and the high brilliance owing to the use of lasers. This method is specifically useful in disordered molecular structures where only a few orientations of the molecules have to be considered. It should be borne in mind, however, that all optical masks must correspond to projections of the disorder model along one specific direction which generates the two-dimensional diffraction picture under consideration. An important disadvantage is caused by the difficulty in simulating the picture of an atom. This situation may be improved by using computer programs with a high-resolution matrix printer representing electron densities by point densities of the printer. This latter method seems to be very powerful because of the possibility of avoiding 'ghosts' in the diffraction picture.

4.2.3.2. *Guideline to solve a disorder problem*

Generally, 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 is predominant, the maximum information can be drawn from the averaged structure. The observations of fractional occupations of lattice sites, split positions and anomalous temperature factors 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).

Difficulties may arise from the intensity integration which should be carried out 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 which 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 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. 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 lead to structure factors for diffuse scattering which are proportional to that 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.

The integrated intensity 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 semi-quantitative interpretation of the essential features of disorder to be realized.

(1) First, it is recommended that the integrated intensities be 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 a superlattice of the structure. An increase of the width of reflections as a function of growing $|\mathbf{H}|$ indicates strained clusters of sub- or superlattice.

(4) The next step is the search for extinction rules of 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 (4.2.2.13)

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

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 = $ integer) for specific values of the reciprocal vector $\mathbf{H}$. If all p_μ are equivalent by symmetry:

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

Other possibilities of 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 semi-quantitative 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 (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 semi-quantitative interpretation is the check of the intensity distribution of diffuse reflections in reciprocal space. Generally 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 diffuse scattering can be determined, a careful check of integrated intensities in the surroundings 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 the information about density effects. Despite the contribution to sharp reflections, one should remember that the information derived from the average structure may be very low (*e.g.* small displacements, low concentrations *etc.*).

(8) As pointed out above, 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. Non-molecular 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 really be found, the use of an atlas of optical transforms (Wooster, 1962; Harburn *et al.*, 1975; Welberry & Withers, 1987) may be very helpful at the beginning of any study of diffuse scattering. 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 the 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 the complete interpretation of the change of the influence of the distribution function on diffraction in the far-angle region.

4.2.4. Quantitative interpretation

4.2.4.1. *Introduction*

In these sections quantitative interpretations of the elastic part of diffuse scattering (X-rays and neutrons) are outlined. Although similar relations are valid, magnetic scattering of neutrons is excluded. Obviously, all disorder phemomena 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 (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 which 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 for 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 provide valuable methods for 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 $Nc V_d$ (N = number of unit cells, c = concentration of defects, V_d = volume of the defect with $V_d > V_c$, V_c = volume of the unit cell) is small in comparison with the total volume $N V_c$ of the crystal, or $V_c \gg c V_d$.

(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 (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 so-called Ising model can hardly be used in order to obtain interaction energies of structural defects. From these remarks it becomes clear that order parameters are more or less 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 of diffuse scattering of 2D disorder by chain-like structures follow. Finally, the 3D case is treated, where formal solutions of the diffraction