4. DIFFUSE SCATTERING AND RELATED TOPICS

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 NcV_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 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 (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

420

problem have been tried and applied successfully to metallic systems to some extent. A short concluding section concerns the special phenomenon of orientational disorder.

4.2.4.2. *One-dimensional disorder of ordered layers*

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 uniquely be determined if a single independent correlation function is active. According to equation (4.2.3.28) Fourier transformation yields the information required. In all other cases a specific model has to be suggested for a full interpretation of diffuse streaks. Another comment seems to be necessary: disorder parameters can be defined uniquely only if the diffraction pattern allows for a differentiation between long-range and short-range order. This question can at least partly be answered by studying the line width of sharp reflections with a very good resolution. Since integrated intensities of sharp reflections have to be separated from the diffuse scattering, this question is of outstanding importance in most cases. Inclusion of diffuse parts in the diffraction pattern during intensity integration of sharp reflections may lead to serious errors in the interpretation of the average structure.

The existence of diffuse streaks in more than one direction of reciprocal space means that the diffraction problem is no longer one-dimensional. Sometimes the problem may be treated independently, if the streaks are sharp, and no interference effects may be observed in the diffraction pattern in areas where the diffuse streaks do overlap. In all other cases there are correlations between the various directions of one-dimensional disorder which may be determined with the aid of a model covering more than one of the pertinent directions of disorder.

Before starting the discussion of the quantitative solution of the one-dimensional problem, some remarks should be made on the usefulness of quantitative disorder parameters. It is well known from statistical thermodynamics that a one-dimensional system cannot show long-range order above $T = 0$ K. Obviously, this statement is in contradiction with many experimental observations where long-range order is realized even in layer structures. The reason for this behaviour is given by the following arguments which are valid for any structure. Let us assume a structure with strong interactions at least in two directions. From the theoretical treatment of the two-dimensional Ising model it is known that such a system shows long-range order below a critical temperature T_c. This statement is true even if the layer is finite, although the strict thermodynamic behaviour is not really critical in the thermodynamical sense. A three-dimensional crystal can be constructed by adding layer after layer. Since each layer has a typical two-dimensional free energy, the full statistics of the three-dimensional crystal may be calculated by introducing a specific free energy for the various stackings of layers. Obviously, this additional energy has to include terms describing potential and entropic energies as well. They may be formally developed into contributions of next, overnext *etc.* nearest neighbours. Apparently, the contribution to

entropy must include configurational and vibrational parts which are strongly coupled. As long as the layers are finite, there is a finite probability of a fault in the stacking sequence of layers which approaches zero with increasing extension of the layers. Consequently, the free energy of a change in the favourite stacking sequence becomes infinite quadratically with the size of the layer. Therefore, the crystal should be either completely ordered or disordered; the latter case can only be realized if the free energies of one or more stacking sequences are exactly equal (very rare, but possible over a small temperature range of phase transformations). An additional positive entropy associated with a deviation from the periodic stacking sequence may lead to a kind of competition between entropy and potential energy, in such a way that periodic sequences of faults result. Obviously, this situation occurs in the transition range of two structures differing only in their stacking sequence. On the other hand, one must assume that defects in the stacking sequence may be realized if the size of the layers is small. This situation occurs during crystal growth, but one should remember that the number of stacking defects should decrease with increasing size of the growing crystal. Apparently, this rearrangement of layers may be suppressed as a consequence of relaxation effects. The growth process itself may influence the propagation of stacking defects and, consequently, the determination of stacking-fault probabilities, aiming at an interpretation of chemical bonding seems to be irrelevant in most cases.

The quantitative solution of the diffraction problem of one-dimensional disorder follows a method similar to the Ising model. As long as next-nearest neighbours alone are considered, the solution is very simple only if two possibilities of structure factors are to be taken into account. Introducing the probability of equal pairs 1 and 2, α, one arrives at the known solution for the *a priori* probability p_μ and *a posteriori* probabilities $p_{\mu\mu'}(\mathbf{m})$, respectively. In the one-dimensional Ising model with two spins and the interaction energies $(U \mp \Delta U)/k_B T$, defining the pair probability $[\alpha = p_{11}(\mathbf{1})]$

$$\alpha = \frac{\exp\{\pm\Delta U/k_B T\}}{[\exp\{+\Delta U/k_B T\} + \exp\{-\Delta U/k_B T\}]}$$

the full symmetry is $p_1 = p_2 = \frac{1}{2}$, and $p_{11}(\mathbf{m}) = p_{22}(\mathbf{m})$.

Consequently:

$$p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) = 1 - p_{11}(\mathbf{m}).$$

The scattered intensity is given by

$$I(\mathbf{H}) = L(h, k) \sum_{\mathbf{m}} \langle FF_m^+ \rangle (N - |m|) \exp\{-2\pi i m l\}, \qquad (4.2.4.1)$$

where $\mathbf{m} = m\mathbf{c}$, N = number of unit cells in the $\mathbf{c}$ direction and $\langle FF^+ \rangle$ depends on λ_1, λ_2 which are the eigenvalues of the matrix

$$\begin{pmatrix} \alpha & 1 - \alpha \\ 1 - \alpha & \alpha \end{pmatrix}.$$

From the characteristic equation

$$\lambda^2 - 2\alpha\lambda - 1 + 2\alpha = 0 \qquad (4.2.4.2)$$

one has

$$\lambda_1 = 1; \quad \lambda_2 = 2\alpha - 1. \qquad (4.2.4.2a)$$

λ_1 describes a sharp Bragg reflection (average structure) which need not be calculated. Its intensity is simply proportional to $\langle F(\mathbf{H}) \rangle$. The second characteristic value yields a diffuse reflection in the same position if the sign is positive ($\alpha > 0.5$), and in a position displaced by $\frac{1}{2}$ in reciprocal space if the sign is negative ($\alpha < 0.5$). Because of the symmetry conditions $p_{11}(\mathbf{m})$ only is needed; it may be determined with the aid of the boundary conditions