

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

$$I \sim \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 + s^2[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.31a)$$

$s = 0$ corresponds to the well known behaviour of sharp reflections, $s = \frac{1}{2}$ (maximum long-range order) gives

$$I \sim \frac{1}{2}[|F_1(\mathbf{H})|^2 + |F_2(\mathbf{H})|^2]. \quad (4.2.3.31b)$$

This result reveals some difficulties for structure determination of the averaged structure as long as s is different from zero or $\frac{1}{2}$, since in the former case the use of integrated sharp Bragg intensities yields a correct average structure. If $s = \frac{1}{2}$, a correct structure determination can only be performed with a refinement allowing for an incoherent superposition of two different structures. Having subtracted all periodic contributions to $p_{\mu\mu'}(\mathbf{r})$, new functions which describe the remaining non-periodic parts have to be introduced (Fig. 4.2.3.6b). In order to obtain a clear overview of intensities, $p'_{\mu\mu'}(\mathbf{r})$ is again defined:

$$p'_{\mu\mu'}(\mathbf{r}) = cp_{\mu\mu'}(\mathbf{r}) - p_{\mu\mu'}(\infty),$$

where c should be chosen such that $p_{\mu\mu'}(\mathbf{0}) = 1$. By this definition a very simple behaviour of the diffuse scattering is obtained:

$$\begin{aligned} p'_{11}(\mathbf{r}) &: \frac{1}{2} - s; & p'_{12}(\mathbf{r}) &: -(\frac{1}{2} - s); \\ p'_{22}(\mathbf{r}) &: \frac{1}{2} + s; & p'_{21}(\mathbf{r}) &: -(\frac{1}{2} + s). \end{aligned}$$

With the definitions introduced above it is found that:

$$p'_{11}(\mathbf{r}) = p'_{22}(\mathbf{r}).$$

The diffuse scattering is given by:

$$I_d(\mathbf{H}) = (\frac{1}{4} - s^2)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2 [P'_{11}(\mathbf{H}) * L(\mathbf{H})]. \quad (4.2.3.32)$$

Since equation (4.2.3.32) is symmetrical with respect to an interchange of F_1 and F_2 , the same result is obtained for I_2 . Diffuse reflections occur in the positions of the sharp ones; the integrated intensities of sharp and diffuse reflections are independent of the special shape of $P'_{11}(\mathbf{H})$: $p_{11}(\mathbf{0}) = 1$; hence

$$1 = \int P'_{11}(\mathbf{H}) \exp\{2\pi i \mathbf{0} \cdot \mathbf{H}\} d\mathbf{H} = \int P'_{11}(\mathbf{H}) d\mathbf{H}.$$

(7) *Lamellar domains with long-range order: tendency to superstructure*

So far it has been tacitly assumed that the crystal shows a preference for equal neighbours. If there is a reversed tendency (pairs of unequal neighbours are more probable) the whole procedure outlined above may be repeated as shown in Fig. 4.2.3.7 for the one-dimensional example. With the same probability of an unlike pair as used for the equal pair in the preceding example, the order process approaches an alternating structure such that the even-order neighbours have the same pair probabilities, while the odd ones are complementary for equal pairs (Fig. 4.2.3.7). In order to calculate intensities, it is necessary to introduce a new lattice with the doubled lattice constant and the corresponding reciprocal lattice with $b^{*'} = b^*/2$. In order to describe the probability $p_{\mu\mu'}(\mathbf{r})$, one has to introduce two lattices in real space – the normal lattice with the

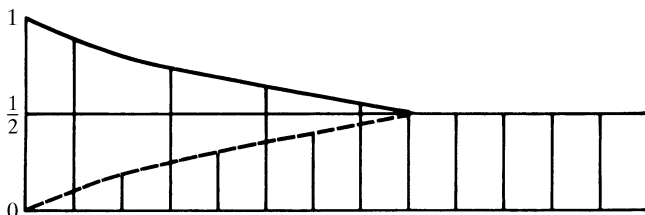


Fig. 4.2.3.7. The same distribution (cf. Fig. 4.2.3.5) in the case of superstructure formation.

undisplaced origin and the displaced one. Fourier transformation of the new functions yields the following very similar results:

Sharp Bragg reflections

(a) $k' = \text{even}$

$$I = \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 \quad (4.2.3.33a)$$

(b) $k' = \text{odd}$

$$I = s^2 \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2 \quad (4.2.3.33b)$$

Diffuse reflections

(c) $k' = \text{odd}$

$$I = (\frac{1}{4} - s^2) \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.33c)$$

Obviously, there is a better situation for determination of the averaged structure which may be performed without any difficulty, regardless of whether s is different from zero or not. For this purpose even reflections (or reflections in the old setting) may be used. The inclusion of odd reflections in the structure determination of the superstructure is also possible if convenient \mathbf{H} -independent scaling factors are introduced in order to compensate for the loss in intensity which is unavoidable for the integration of the diffuse scattering.

A few comments should be made on the physical meaning of the formulae derived above. All formulae may be applied to the general three-dimensional case, where long-range and short-range order is a function of the relevant thermodynamical parameters. In practice, long-range order will never be realized in a real crystal consisting of mosaic blocks which may behave as small subunits in order-disorder transitions. Another reason to assume partly incoherent areas in single crystals is the presence of possible strains or other distortions at the interfaces between domains which should cause a decrease of the averaged areas of coherent scattering. All these effects may lead to diffuse scattering in the neighbourhood of Bragg peaks, similar to the diffuse scattering caused by domain structures. For this reason an incoherent treatment of domains is probably more efficient, although considerable errors in intensity measurements may occur. A very careful study of line profiles is generally useful in order to decide between the various possibilities.

(8) *Order-disorder in three dimensions*

Correlation functions in three dimensions may have very complicated periodicities; hence a careful study is necessary as to 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 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 (superlattice) in reciprocal space; in real space this means a convolution with the Fourier transform of this lattice (sublattice). In this way the averaged structure is generated in each of the subcells (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' which 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 supergroup is lower in general, all missing