

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

tered by the atomic nuclei (we are disregarding magnetic interactions in this chapter), *i.e.* X-rays probe the distribution of charges, which (in particular for light atoms) may not coincide with that of the nuclei. This fact forms the basis for the well known X – N technique in the analysis of Bragg intensities. No such studies of disorder diffuse scattering have been performed up to now, but may be a challenge for the future. As a consequence of the different size of the scattering objects, the scattering amplitude falls off with increasing scattering vector  $|\mathbf{H}| = (\sin\theta)/\lambda$  for X-rays (the form factor), while it is constant for neutrons. Since for a complete interpretation of diffuse scattering high  $Q$  values are generally required, neutrons have their advantages in this respect. The scattering intensity varies as  $Z^2$  ( $Z$  = number of electrons) for X-rays and more-or-less erratically for neutrons, for which it also depends on the specific isotope. This imposes problems for X-rays when trying to detect light elements (in particular H and O) in the presence of heavy elements or discriminating neighbouring elements in the periodic table (*e.g.* Al/Si/Mg, Fe/Co/Ni). On the other hand, these differences in scattering power can be used to identify the atomic species taking part in the disorder by comparing the intensity distributions observed with both methods. The contrast can be further enhanced by marking selected atoms by isotope substitution for neutrons or by using anomalous dispersion for X-rays.

In many practical cases, the complementarities of the two methods can be exploited by using them simultaneously. Some illustrative examples can be found in Boysen & Frey (1998).

Another important difference is in the energies given by the dispersion laws  $E_x = \hbar ck$  and  $E_n = (\hbar^2/2m)k^2$  for X-rays and neutrons, respectively, where  $c$  is the velocity of light,  $m$  is the neutron mass and  $k = 2\pi/\lambda$  is the wavevector. For a typical wavelength,  $\lambda = 1.54 \text{ \AA}$  (Cu  $K\alpha$ ) ( $k = 4.08 \text{ \AA}^{-1}$ ),  $E_x = 8 \text{ keV}$  and  $E_n = 35 \text{ meV}$ , *i.e.* the energies differ by almost six orders of magnitude. This means that neutron energies are similar to those of typical collective lattice excitations, which may therefore be determined more easily by neutron spectroscopy. The basic question of whether the underlying disorder is of static or dynamic origin can be answered using neutrons alone, *e.g.* by comparing the ‘integral’ (= elastic + inelastic) scattered intensity (*i.e.* without energy analysis, using a two-axis diffractometer) with the purely elastic intensity by placing an analyser crystal set to zero energy transfer in the diffracted beam (using a triple-axis diffractometer) or using time-of-flight methods. The high energy resolution of Mössbauer radiation can also be used for this purpose. Owing to the very low available intensities, however, this technique has only been applied occasionally. In the elastic mode, diffracted neutron intensities are also usually rather weak. The decision can, however, also be made simply by comparing the positions of the intensity maxima in reciprocal space. This follows from a consideration of the relative changes of the momentum transfer (the wavevector) in the two cases. For example, for an energy change  $\Delta E = E_f - E_i$  (the subscripts refer to final and incident energies) of 1 meV, one obtains a change in the scattered wavevector  $\Delta k_f$  of  $2 \times 10^{-6} \text{ \AA}^{-1}$  for X-rays and  $0.06 \text{ \AA}^{-1}$  for neutrons. In a two-axis experiment where the detector does not discriminate energies, *i.e.* without prior knowledge of the real energies, the distribution of diffuse intensities has to be drawn as if the scattering had been elastic ( $\Delta E = 0$ ). In other words, the signal appears at a position displaced by  $\Delta k_f$ . From the estimations above it is clear that only in the neutron case can a measurable effect be expected.

Other specific features of neutrons include their magnetic moment (magnetic scattering is still a domain of neutrons, although progress is now being made with synchrotron radiation) and (nuclear) spin and isotope incoherent scattering processes (which allow the determination of the self-correlation functions). It is possible to separate the spin-incoherent part and distinguish between nuclear and magnetic scattering using polarization analysis. For most elements scattering and absorption is much

weaker for neutrons, allowing larger samples to be analysed and sample environments (furnaces, pressure cells, electric and magnetic fields, special atmospheres *etc.*) to be handled much more easily. Differences in the experimental techniques for X-ray and neutron scattering are discussed in Section 4.2.8.

## 4.2.3. Qualitative treatment of structural disorder

## 4.2.3.1. Basic mathematics

Any structure analysis of disordered structures should start with a qualitative interpretation of diffuse scattering. This may be achieved with the aid of Fourier transforms and convolutions. A thorough mathematical treatment of Fourier transforms is given in Chapter 1.3 of this volume; here we give a simple short overview of the practical use of Fourier transforms, convolutions, their algebraic operations and examples of functions which are frequently used in diffraction physics (see, *e.g.*, Patterson, 1959; Jagodzinski, 1987). For simplicity, the following modified notation is used in this section: functions in real space are represented by lower-case letters, *e.g.*  $a(\mathbf{r})$ ,  $b(\mathbf{r})$ , ... except for  $F(\mathbf{r})$  [also, more frequently, denoted as  $\rho(\mathbf{r})$ ] and  $P(\mathbf{r})$ , which are used as general symbols for a structure and the Patterson function, respectively; functions in reciprocal space are represented by capital letters  $A(\mathbf{H})$ ,  $B(\mathbf{H})$ ; and  $\mathbf{r}$  and  $\mathbf{H}$  are general vectors in real and reciprocal space, respectively.  $H$ ,  $K$ ,  $L$  denote continuous variables in reciprocal space; integer values are given by the commonly used symbols  $h$ ,  $k$ ,  $l$ .  $Hx + Ky + Lz$  is the scalar product  $\mathbf{H} \cdot \mathbf{r}$ ;  $d\mathbf{r}$  and  $d\mathbf{H}$  indicate integrations in three dimensions in real and reciprocal space, respectively. Even for X-rays, the electron density  $\rho(\mathbf{r})$  will generally be replaced by the scattering potential  $a(\mathbf{r})$ . Consequently, anomalous contributions to scattering may be included if complex functions  $a(\mathbf{r})$  are admitted. In the neutron case  $a(\mathbf{r})$  refers to a quasi-potential. Using this notation we obtain the scattered amplitude

$$A(\mathbf{H}) = \int_{\mathbf{r}} a(\mathbf{r}) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{r}, \quad (4.2.3.1a)$$

$$a(\mathbf{r}) = \int_{\mathbf{H}} A(\mathbf{H}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{H} \quad (4.2.3.1b)$$

(constant factors are omitted).

$a(\mathbf{r})$  and  $A(\mathbf{H})$  are reversibly and uniquely determined by Fourier transformation. Consequently, equations (4.2.3.1) may simply be replaced by  $a(\mathbf{r}) \leftrightarrow A(\mathbf{H})$ , where the double-headed arrow represents the two integrations given by (4.2.3.1) and means:  $A(\mathbf{H})$  is the Fourier transform of  $a(\mathbf{r})$  and *vice versa*. The following relations may easily be derived from (4.2.3.1):

$$a(\mathbf{r}) + b(\mathbf{r}) \leftrightarrow A(\mathbf{H}) + B(\mathbf{H}) \quad (\text{law of addition}), \quad (4.2.3.2)$$

$$\beta a(\mathbf{r}) \leftrightarrow \beta A(\mathbf{H}) \quad (\text{law of scalar multiplication}), \quad (4.2.3.3)$$

where  $\beta$  is a scalar quantity.

On the other hand, the multiplication of two functions does not yield a relation of similar symmetrical simplicity:

$$\begin{aligned} a(\mathbf{r})b(\mathbf{r}) &\leftrightarrow \int A(\mathbf{H}')B(\mathbf{H} - \mathbf{H}') d\mathbf{H}' \\ &= A(\mathbf{H}) * B(\mathbf{H}), \end{aligned} \quad (4.2.3.4a)$$

$$\begin{aligned} a(\mathbf{r}) * b(\mathbf{r}) &= \int a(\mathbf{r}')b(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\ &\leftrightarrow A(\mathbf{H})B(\mathbf{H}) \end{aligned} \quad (4.2.3.4b)$$

(the laws of convolution and multiplication).

For simplicity, the complete convolution integral is abbreviated as  $a(\mathbf{r}) * b(\mathbf{r})$ . Since  $a(\mathbf{r})b(\mathbf{r}) = b(\mathbf{r})a(\mathbf{r})$ ,

$$\int A(\mathbf{H}')B(\mathbf{H} - \mathbf{H}') d\mathbf{H}' = \int B(\mathbf{H}')A(\mathbf{H} - \mathbf{H}') d\mathbf{H}'$$

and *vice versa*. The convolution operation is commutative in either space.

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

The distribution law  $a(b + c) = ab + ac$  is valid for the convolution as well:

$$a(\mathbf{r}) * [b(\mathbf{r}) + c(\mathbf{r})] = a(\mathbf{r}) * b(\mathbf{r}) + a(\mathbf{r}) * c(\mathbf{r}). \quad (4.2.3.5)$$

The associative law of multiplication does not hold if mixed products (convolution and multiplication) are used:

$$a(\mathbf{r}) * [b(\mathbf{r})c(\mathbf{r})] \neq [a(\mathbf{r}) * b(\mathbf{r})]c(\mathbf{r}). \quad (4.2.3.6)$$

From equations (4.2.3.1) one has

$$\begin{aligned} a(\mathbf{r} - \mathbf{r}_0) &\leftrightarrow A(\mathbf{H}) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_0\}, \\ A(\mathbf{H} - \mathbf{H}_0) &\leftrightarrow a(\mathbf{r}) \exp\{-2\pi i \mathbf{H}_0 \cdot \mathbf{r}\} \end{aligned} \quad (4.2.3.7)$$

(the law of displacements).

Since symmetry operations are well known to crystallographers in reciprocal space as well, the law of inversion is only mentioned here:

$$a(-\mathbf{r}) \leftrightarrow A(-\mathbf{H}). \quad (4.2.3.8)$$

Consequently, if  $a(\mathbf{r}) = a(-\mathbf{r})$ , then  $A(\mathbf{H}) = A(-\mathbf{H})$ . In order to calculate the intensity, the complex conjugate  $A^+(\mathbf{H})$  is needed:

$$a^+(\mathbf{r}) \leftrightarrow A^+(-\mathbf{H}), \quad (4.2.3.9a)$$

$$a^+(-\mathbf{r}) \leftrightarrow A^+(\mathbf{H}). \quad (4.2.3.9b)$$

Equations (4.2.3.9) yield the relationship  $A^+(-\mathbf{H}) = A(\mathbf{H})$  ('Friedel's law') if  $a(\mathbf{r})$  is a *real* function. The multiplication of a function with its conjugate is given by

$$a(\mathbf{r}) * a^+(-\mathbf{r}) \leftrightarrow |A(\mathbf{H})|^2,$$

with

$$a(\mathbf{r}) * a^+(-\mathbf{r}) = \int a(\mathbf{r}') a(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P(\mathbf{r}). \quad (4.2.3.10)$$

Note that  $P(\mathbf{r}) = P(-\mathbf{r})$  is not valid if  $a(\mathbf{r})$  is complex. Consequently  $|A(-\mathbf{H})|^2 \neq |A(\mathbf{H})|^2$ . This is shown by evaluating  $A(-\mathbf{H})A^+(-\mathbf{H})$ ,

$$A(-\mathbf{H})A^+(-\mathbf{H}) \leftrightarrow a(-\mathbf{r}) * a^+(\mathbf{r}) = P(-\mathbf{r}). \quad (4.2.3.11)$$

Equation (4.2.3.11) is very useful for the determination of the contribution of anomalous scattering to diffuse reflections.

Most of the diffuse-diffraction phenomena observed may be interpreted qualitatively or even semiquantitatively in a very simple manner using a limited number of important Fourier transforms, which are given below.

##### 4.2.3.2. Fourier transforms

###### (1) Normalized Gaussian function

$$(\pi^{3/2} \alpha \beta \gamma)^{-1} \exp\{-(x/\alpha)^2 - (y/\beta)^2 - (z/\gamma)^2\}. \quad (4.2.3.12)$$

This plays an important role in statistics. Its Fourier transform is again a Gaussian:

$$\exp\{-\pi^2(\alpha^2 H^2 + \beta^2 K^2 + \gamma^2 L^2)\}. \quad (4.2.3.12a)$$

The three parameters  $\alpha, \beta, \gamma$  determine the width of the curve. Small values of  $\alpha, \beta, \gamma$  represent a broad maximum in reciprocal space but a narrow one in real space and *vice versa*. The constant has been chosen such that the integral of the Gaussian is unity in real space. The product of two Gaussians in reciprocal space,

$$\begin{aligned} &\exp\{-\pi^2(\alpha_1^2 H^2 + \beta_1^2 K^2 + \gamma_1^2 L^2)\} \\ &\times \exp\{-\pi^2(\alpha_2^2 H^2 + \beta_2^2 K^2 + \gamma_2^2 L^2)\} \\ &= \exp\{-\pi^2[(\alpha_1^2 + \alpha_2^2)H^2 + (\beta_1^2 + \beta_2^2)K^2 \\ &\quad + (\gamma_1^2 + \gamma_2^2)L^2]\} \end{aligned} \quad (4.2.3.12b)$$

again represents a Gaussian of the same type, but with a sharper profile. Consequently, its Fourier transform, which is given by the convolution of the transforms of the two Gaussians, is itself a Gaussian with a broader maximum. It may be concluded from this discussion that the Gaussian with  $\alpha, \beta, \gamma \rightarrow 0$  is a  $\delta$  function in real space and its Fourier transform is unity in reciprocal space.

###### (2) $\delta$ 'functions'

For a proper definition see, e.g., Cowley (1981). Here the term is used with the relaxed definition  $\delta(\mathbf{r}) = 1$  if  $\mathbf{r} = 0$  and zero elsewhere.

$$\delta(\mathbf{r}) \leftrightarrow 1 \text{ and } \delta(\mathbf{H}) \leftrightarrow 1$$

and

$$\delta(\mathbf{r} - \mathbf{r}_0) \leftrightarrow \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_0\}.$$

The convolution of two  $\delta$  functions is again a  $\delta$  function.

###### (3) Lattices

Lattices in real and reciprocal space may be described by  $\delta$  functions:

$$l(\mathbf{r}) = \sum_{\mathbf{n}} \delta(\mathbf{r} - \mathbf{n})$$

and

$$L(\mathbf{H}) = \sum_{\mathbf{h}} \delta(\mathbf{H} - \mathbf{G}),$$

where  $\mathbf{n} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$  and  $\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$  represent the components of the translation vectors in real and reciprocal space, respectively. The Fourier transforms of lattices with orthogonal basis vectors of unit length and an infinite number of points in all three dimensions correspond to each other. In the following the relation  $l(\mathbf{r}) \leftrightarrow L(\mathbf{H})$  is used in this generalized sense.

The Fourier transforms of *finite* lattices with  $N_1, N_2, N_3$  nodes in the basic directions  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  are given by

$$\frac{\sin \pi N_1 H}{\sin \pi H} \frac{\sin \pi N_2 K}{\sin \pi K} \frac{\sin \pi N_3 L}{\sin \pi L}, \quad (4.2.3.13)$$

which is a periodic function in reciprocal space, but, strictly speaking, nonperiodic in real space. It should be pointed out that the correspondence of lattices in either space is valid only if the origin coincides with a  $\delta$  function. This fact may easily be understood by applying the law of displacement given in equation (4.2.3.7).

###### (4) Box functions

The Fourier transform of a box function  $b(\mathbf{r})$  with unit height is

$$b(\mathbf{r}) \leftrightarrow \frac{\sin \pi \alpha H}{\pi H} \frac{\sin \pi \beta K}{\pi K} \frac{\sin \pi \gamma L}{\pi L}. \quad (4.2.3.14)$$

$\alpha, \beta, \gamma$  describe its extension in the three dimensions. This function is real as long as the centre of symmetry is placed at the origin, otherwise the law of displacement has to be used. The convolution of the box function with its inverse is needed for the calculation of intensities:

$$\begin{aligned} t(\mathbf{r}) &= b(\mathbf{r}) * b(-\mathbf{r}) \\ &\leftrightarrow \left( \frac{\sin \pi \alpha H}{\pi H} \right)^2 \left( \frac{\sin \pi \beta K}{\pi K} \right)^2 \left( \frac{\sin \pi \gamma L}{\pi L} \right)^2. \end{aligned} \quad (4.2.3.15)$$

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

$l(\mathbf{r})$  is a generalized three-dimensional 'pyramid' of doubled basal length when compared with the corresponding length of the box function. The top of the pyramid has a height given by the number of unit cells covered by the box function. Obviously, the box function generates a particle size in real space by multiplying the infinite lattice  $l(\mathbf{r})$  by  $b(\mathbf{r})$ . Fourier transformation yields a particle-size effect well known in diffraction. Correspondingly, the termination effect of a Fourier synthesis is caused by multiplication by a box function in reciprocal space, which causes a broadening of maxima in real space.

### (5) Convolutions

It is often very useful to elucidate the convolution given in equations (4.2.3.4) by introducing the corresponding pictures in real or reciprocal space. Since  $1 \cdot f(\mathbf{r}) = f(\mathbf{r})$ ,  $\delta(\mathbf{H}) * F(\mathbf{H}) = F(\mathbf{H})$ , the convolution with a  $\delta$  function must result in an identical picture of the second function, although the function is used as  $f(-\mathbf{r})$  in the integrals of equations (4.2.3.4),  $f(\mathbf{r} - \mathbf{r}')$  with  $\mathbf{r}'$  as variable in the integral of convolution. The convolution with  $f(-\mathbf{r})$  brings the integral into the form

$$\int f(\mathbf{r}')f(\mathbf{r}' - \mathbf{r}) d\mathbf{r}', \quad (4.2.3.16)$$

which is known as the Patterson (or self- or auto-convolution) function and represents the generalized Patterson function including anomalous scattering [cf. equation (4.2.3.10)].

The change of the variable in the convolution integral may sometimes lead to confusion if certain operations are applied to the arguments of the functions entering the integral. Hence it is useful to mention the invariance of the convolution integral with respect to a change of sign, or a displacement, respectively, if applied to  $\mathbf{r}'$  in both functions. Consequently, the convolution with the inverted function  $a(\mathbf{r}) * b(-\mathbf{r})$  may be determined as follows:

$$\begin{aligned} b'(\mathbf{r}) &= b(-\mathbf{r}), \\ a(\mathbf{r}) * b(-\mathbf{r}) &= a(\mathbf{r}) * b'(\mathbf{r}) = \int a(\mathbf{r}')b'(\mathbf{r} - \mathbf{r}') d\mathbf{r}', \\ &= \int a(\mathbf{r}')b(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P'(\mathbf{r}). \end{aligned} \quad (4.2.3.17)$$

This equation means that the second function is displaced into the positive direction by  $\mathbf{r}$ , then multiplied by the first function and integrated. In the original meaning of the convolution, the operation represents a displacement of the second function in the positive direction and an inversion at the displaced origin before multiplication and subsequent integration. On comparing the two operations it may be concluded that  $P'(\mathbf{r}) \neq P'(-\mathbf{r})$  if the second function is acentric. For real functions both have to be acentric. In a similar way, it may be shown that the convolution

$$\begin{aligned} a(\mathbf{r} - \mathbf{m}) * b(\mathbf{r} - \mathbf{m}') &= \int_{\mathbf{r}'} a(\mathbf{r}' - \mathbf{m})b(\mathbf{r} - \mathbf{m}' - \mathbf{r}') d\mathbf{r}' \\ &= \int_{\mathbf{r}''} a(\mathbf{r}'')b(\mathbf{r} - \mathbf{m}' - \mathbf{m} - \mathbf{r}'') d\mathbf{r}''. \end{aligned} \quad (4.2.3.18)$$

Equation (4.2.3.18) indicates a displacement by  $\mathbf{m}' + \mathbf{m}$  with respect to the convolution of the undisplaced functions. Consequently,

$$\delta(\mathbf{r} - \mathbf{m}) * \delta(\mathbf{r} - \mathbf{m}') = \delta(\mathbf{r} - \mathbf{m} - \mathbf{m}'). \quad (4.2.3.19)$$

Obviously, the commutative law of convolution is obeyed; on the other hand, the convolution with the inverted function yields

$$\delta(\mathbf{r} - \mathbf{m}' + \mathbf{m}),$$

indicating that the commutative law (interchange of  $\mathbf{m}$  and  $\mathbf{m}'$ ) is violated because of the different signs of  $\mathbf{m}$  and  $\mathbf{m}'$ .

The effectiveness of the method outlined above may be greatly improved by introducing further Fourier transforms of useful functions in real and reciprocal space (Patterson, 1959).

### 4.2.3.3. General formulation of a disorder problem

From these basic concepts the generally adopted method in a disorder problem is to try to separate the scattering intensity into two parts, namely one part  $\langle \rho \rangle$  from an average periodic structure where formulae (4.2.2.10), (4.2.2.11) apply and a second part  $\Delta \rho$  resulting from fluctuations from this average (see, e.g., Schwartz & Cohen, 1977). One may write this formally as

$$\rho = \langle \rho \rangle + \Delta \rho, \quad (4.2.3.20)$$

where  $\langle \rho \rangle = \langle \rho_c \rangle * l$  is defined to be time-independent and periodic in space and  $\langle \Delta \rho \rangle = 0$ .  $\langle \rho_c \rangle = (1/N) \sum_i \rho_i$  is the density of the average unit cell obtained by the projection of all unit cells into a single one. Fourier transformation gives the average amplitude,

$$\langle A \rangle = \langle F \rangle L = \sum_i \langle F \rangle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_i\}, \quad (4.2.3.21a)$$

where  $\langle F \rangle$  is the usual structure factor (4.2.2.11). The difference structure  $\Delta \rho$  leads to the difference amplitude,

$$\begin{aligned} \Delta A &= A - \langle A \rangle = \sum_i (F_i - \langle F \rangle) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_i\} \\ &= \sum_i \Delta F_i \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_i\}. \end{aligned} \quad (4.2.3.21b)$$

Because cross terms  $\langle \rho \rangle * \Delta \rho$  vanish by definition, the Patterson function is

$$\begin{aligned} [\langle \rho(\mathbf{r}) \rangle + \Delta \rho(\mathbf{r})] * [\langle \rho(-\mathbf{r}) \rangle + \Delta \rho(-\mathbf{r})] \\ = [\langle \rho(\mathbf{r}) \rangle * \langle \rho(-\mathbf{r}) \rangle] + [\Delta \rho(\mathbf{r}) * \Delta \rho(-\mathbf{r})]. \end{aligned} \quad (4.2.3.22)$$

Fourier transformation gives

$$I \simeq |\langle F \rangle|^2 + |\Delta F|^2, \quad (4.2.3.23a)$$

$$|\Delta F|^2 \simeq \langle |F|^2 \rangle - |\langle F \rangle|^2. \quad (4.2.3.23b)$$

Since  $\langle \rho \rangle$  is periodic, the first term in (4.2.3.23a) describes Bragg scattering,

$$I_B = \langle A \rangle \langle A^* \rangle = |\langle F \rangle|^2 L, \quad (4.2.3.24)$$

where  $\langle F \rangle$  plays the normal role of a structure factor of one cell of the averaged structure. The second term corresponds to diffuse scattering,

$$I_D = \langle \Delta A \Delta A^* \rangle = \left\langle \sum_i \sum_j \Delta F_i \Delta F_j^* \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_i - \mathbf{r}_j)\} \right\rangle. \quad (4.2.3.25)$$

In many cases, diffuse interferences are centred exactly at the positions of the Bragg reflections. It is then a serious experimental problem to decide whether the observed intensity distribution is due to Bragg scattering obscured by crystal-size limitations or due to other scattering phenomena.

If disordering is exclusively time-dependent,  $\langle \rho \rangle$  represents the time average, whereas  $\langle F \rangle$  gives the pure elastic scattering part [cf. (4.2.2.8)] and  $\Delta F$  refers to inelastic scattering only.

### 4.2.3.4. General aspects of diffuse scattering

Diffuse scattering may be classified in various ways which may be related to specific aspects of the intensity distribution, e.g. according to the type of disorder: substitutional (or density or chemical) or displacive. The general expression (4.2.3.25), which may be rewritten as

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

$$I_D = \left\langle \sum_k \left( \sum_i \Delta F_i \Delta F_{i+k} \right) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_k\} \right\rangle \\ = \sum_k \langle \Delta F \Delta F^* \rangle_k \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_k\}, \quad (4.2.3.26)$$

where  $\mathbf{r}_k = \mathbf{r}_i - \mathbf{r}_j$ , contains the difference structure factor  $\Delta F$ , which may formally be written as

$$\Delta F = (\Delta f) \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r} + \Delta \mathbf{r})\},$$

where  $(\Delta f)$  denotes a fluctuation of the scattering density (the form factor in the case of X-rays and the scattering length in the case of neutrons; note that this may include vacancies) and  $\Delta \mathbf{r}$  denotes a fluctuation of the position, *i.e.* they refer to substitutional and displacive disorder, respectively. Although the two types often occur together in real crystals, they may be discriminated through their different dependence on the modulus of the scattering vector  $\mathbf{H}$ . This may be seen by considering the diffuse scattering of completely random fluctuations, *i.e.* without any correlations. For substitutional disorder one easily derives from (4.2.3.26)

$$I_D = N \langle \Delta F^2 \rangle = N \langle \Delta f^2 \rangle,$$

while for displacive fluctuations with small amplitudes  $\Delta \mathbf{r}$  the exponential may be expanded:

$$\exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{r}_i\} \simeq (1 + 2\pi i \mathbf{H} \cdot \Delta \mathbf{r}_i + \dots),$$

leading to

$$I_D = N f^2 \sum_k \sum_i (2\pi i \mathbf{H} \cdot \Delta \mathbf{r}_i) (2\pi i \mathbf{H} \cdot \Delta \mathbf{r}_{i+k}) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_k\} \quad (4.2.3.27)$$

and

$$I_D = N f^2 4\pi^2 H^2 \langle \Delta r_i^2 \rangle. \quad (4.2.3.28)$$

Hence in the substitutional case the diffuse intensity is constant throughout reciprocal space, while in the displacive case it increases with  $H^2$ , *i.e.* it is zero near the origin. Any correlations will modulate this intensity, but will not change this general behaviour.

A second classification is related to the dimensionality of the disorder: one-dimensional disorder between two-dimensionally ordered objects (planes) leading to diffuse streaks perpendicular to the planes, two-dimensional disorder between one-dimensionally ordered objects (chains) leading to diffuse planes and general three-dimensional disorder.

These different types of disorder will be further discussed separately in the next paragraphs.

From the derivation in Section 4.2.3.3, one may note that information about an averaged disordered structure is contained in the Bragg scattering governed by

$$\langle F \rangle = \sum_i n_i f_i \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_i\} T_i(\mathbf{H}), \quad (4.2.3.29)$$

where  $T_i(\mathbf{H})$  is the Debye–Waller factor. Back-transformation to real space gives

$$\langle \rho \rangle = \sum_i n_i f_i \delta(\mathbf{r} - \mathbf{r}_i) * \text{p.d.f.}(\mathbf{r} - \mathbf{r}_i), \quad (4.2.3.30)$$

*i.e.* each average position is convoluted with p.d.f. $(\mathbf{r} - \mathbf{r}_i)$ , the probability density function, which is the Fourier transform of  $T_i(\mathbf{H})$ . Any disorder model derived from the diffuse scattering must therefore comply with the p.d.f., *i.e.* this may and should be used to validate these models.

##### 4.2.3.5. Types of diffuse scattering

###### 4.2.3.5.1. Substitutional fluctuations, occupational disorder

As mentioned above, a completely random distribution of chemical species leads to a uniform distribution of diffuse intensity, which is also called monotonic Laue scattering. For example, for a binary alloy with scattering densities  $f_1$  and  $f_2$  and concentrations  $c_1$  and  $c_2$  this is simply given by  $I_D \propto c_1 c_2 (f_1 - f_2)^2$ . Several authors use this, *i.e.* the intensity of a random distribution of occupancies, to define a so-called Laue unit, and therewith to put the general diffuse scattering on a relative scale.

Any deviations from the monotonic Laue scattering may be due either to the scattering factor of the objects (*e.g.* molecules) or to short-range-order correlations. For example, for a simple defect pair with distance  $\mathbf{R}$  we have

$$I_D \propto c_1 c_2 (f_1 - f_2)^2 [1 + \cos(2\pi \mathbf{H} \cdot \mathbf{R})], \quad (4.2.3.31a)$$

or for more general short-range order

$$I_D \propto c_1 c_2 (f_1 - f_2)^2 \sum_n \alpha_n \cos(2\pi \mathbf{H} \cdot \mathbf{r}_n), \quad (4.2.3.31b)$$

where  $\alpha_n$  are Warren–Cowley short-range-order parameters, as will be discussed in more detail in Section 4.2.5.4.

For a periodic modulation  $\Delta f_n = f_A \cos(2\pi \mathbf{K} \cdot \mathbf{r}_n)$

$$I_D \propto f_A^2 \left| \sum_n [\exp\{2\pi i (\mathbf{H} + \mathbf{K}) \cdot \mathbf{r}_n\} + \exp\{2\pi i (\mathbf{H} - \mathbf{K}) \cdot \mathbf{r}_n\}] \right|^2 \\ \propto f_A^2 \sum_G \delta(\mathbf{H} - \mathbf{G} \pm \mathbf{K}), \quad (4.2.3.32)$$

where  $\mathbf{G}$  is a reciprocal-lattice vector.

Hence a harmonic 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  $\mp 2\pi \Phi$ . The reciprocal lattice may then be written in the following form:

$$L(\mathbf{H}) + \frac{\alpha}{2} L(\mathbf{H} + \Delta \mathbf{H}) \exp\{2\pi i \Phi\} \\ + \frac{\alpha}{2} L(\mathbf{H} - \Delta \mathbf{H}) \exp\{2\pi i (-\Phi)\}, \quad (4.2.3.33)$$

where  $0 \leq \alpha \leq 1$ . Fourier transformation yields

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

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 no  $n \Delta \mathbf{H}$  ( $n = \text{integer}$ ) coincides 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

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

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).

### 4.2.3.5.2. Displacement fluctuations, displacive disorder

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. Formally, a periodic modulation  $\Delta \mathbf{r}_n = \mathbf{a} \cos(2\pi \mathbf{K} \cdot \mathbf{r}_n)$  leads to

$$I_D \propto (2\pi \mathbf{H} \cdot \mathbf{a})^2 \sum_{\mathbf{G}, \nu} A_\nu \delta(\mathbf{H} - \mathbf{G} \pm \nu \mathbf{K}), \quad (4.2.3.35)$$

where  $\mathbf{a}$  is the amplitude of the displacement wave with  $\mathbf{a} = \alpha \mathbf{e}$  and  $\mathbf{e}$  is the polarization vector:  $|\mathbf{e}| = 1$ . Equation (4.2.3.35) denotes a set of satellites whose amplitudes are described by Bessel functions of  $\nu$ th order, where  $\nu$  represents the order of the satellites. The intensity of the satellites increases with the magnitude of the product  $\mathbf{H} \cdot \mathbf{a}$ . 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' (*i.e.* periods) cause a broadening of satellites in reciprocal space but no change in their integrated intensities as long as the changes are not correlated with fluctuation periods. The broadening of satellite reflections increases with the order of the 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.

### 4.2.3.5.3. Clusters and domains

Many disorder problems may be treated qualitatively in terms of coarsened structures that are made up of clusters or domain-like order extending along one or more directions in space. Common crystals are made up of 'mosaic individuals' which are separated irregularly by unspecified defects such as dislocations, small-angle boundaries, micro-strain fields and other defects. This 'real' crystallinity is not covered by the term 'disorder'. Clustering is, in a structural sense, not a very well defined term, but refers to general agglomerations of atoms, vacancies, defects or atomic groups due to preferred chemical bonding or due to some kind of exsolution processes. In general, the term 'cluster' is used to describe some inhomogeneity in a basic matrix structure. The term 'domain' usually implies either a spatially varying structure forming separate blocks, such as occurring in twin domains, or a spatial variation of a physical property (*e.g.* magnetic moment), which may be visualized by different configurations (see, *e.g.*, Frey, 1997). Structural domains may be chemically homogeneous, as is the case in twin domain structures, or heterogeneous, which occurs, *e.g.*, in feldspars with their complicated Ca/Na and Al/Si distributions. A definition of a domain structure may be given by symmetry arguments or, equivalently, by the order-parameter concept. Individual domains of the coarsened structure may be derived from a, possibly hypothetical, high-symmetry aristophase obeying the concept of symmetry groups. A lower symmetry of the domain is either due to loss of a point-group symmetry element (twin domains) or due to loss of a translational symmetry element of the aristophase, giving rise to the formation of out-of-

phase domains. The special case of antiphase domains is related to a violation of a translational vector  $\mathbf{t}$  in the aristophase by regular or irregular insertion of lattice displacements  $\frac{1}{2}\mathbf{t}$ . Shear domains, which are related by other fractional parts of  $\mathbf{t}$ , may be explained by cooperative gliding of structural building blocks, for example coordination polyhedra. Colour (black-and-white) symmetry has to be used for magnetic domain structures and may also be used for chemical domain ordering. While preserving the same lattice, the disordered (usually high-temperature) phase, which is specified by grey, decomposes into black and white domains, possibly embedded in the grey matrix. However, the term 'atomic cluster' is frequently used in this context. Domains can exhibit a new order by themselves, thus creating new symmetries of the superstructure. The boundaries between different domains are apparently essential and may even be used for a definition of a domain. This does not mean that the boundaries or domain walls are simple atomic planes rather than extended intermediate structural states which mellow the transition from one domain to the next one. Thus extended walls may carry a 'gradient' structure between neighbouring differently oriented domains and may be treated as new domains with their own structure. If misfits at the planes of coincidence are accompanied by remarkable straining, an array of dislocations may destroy the exact symmetry relation between the individuals. There is a stepwise transition from fully coherent domains to fully incoherent crystal parts. As long as coherency between the individuals is preserved, domain structures can be treated simply by means of Fourier transforms and characteristic features of the disorder problem may be extracted from diffuse patterns.

Quite generally, the scattering density for a general arrangement of domains may be written as (Boysen, 1995; Frey, 1997)

$$[\rho_1 * l_1][b_1^1 * d_1^1 + b_1^2 * d_1^2 + \dots] + [\rho_2 * l_2][b_2^1 * d_2^1 + b_2^2 * d_2^2 + \dots] + \dots, \quad (4.2.3.36)$$

where  $\rho_i = \rho_i(\mathbf{r})$  is the structure of the unit cell of domain  $i$ ,  $l_i(\mathbf{r})$  is the lattice function,  $b_i^j(\mathbf{r})$  is the shape function (which is unity in the region of domain  $i$  with size  $j$  and zero elsewhere) and  $d_i^j(\mathbf{r}) = \sum \delta(\mathbf{r} - \mathbf{m}_i^j)$  is the distribution function ( $\mathbf{m}_i^j$  are the centres of the domains). Note again that domain walls may be included in this formulation as separate 'domains'. Fourier transformation yields the scattering amplitude

$$[F_1 L_1] * [B_1^1 D_1^1 + B_1^2 D_1^2 + \dots] + [F_2 L_2] * [B_2^1 D_2^1 + B_2^2 D_2^2 + \dots] + \dots, \quad (4.2.3.37)$$

where  $F_i = F_i(\mathbf{H})$  is the usual structure factor,  $L_i(\mathbf{H})$  is the lattice function in reciprocal space,  $B_i^j(\mathbf{H})$  and  $D_i^j(\mathbf{H})$  are the Fourier transforms of the shape and distribution function, respectively, and the intensity is

$$\sum_i |[F_i L_i] * [\sum_j B_i^j D_i^j]|^2 + 2 \sum_{i \neq k} [F_i L_i] * [\sum_j B_i^j D_i^j] [F_k^+ L_k^+] * [\sum_j B_k^{j+} D_k^{j+}]. \quad (4.2.3.38)$$

The first term represents sharp or diffuse reflections that are modified by the convolution with the Fourier transforms of the shape and distribution function (more correctly, with the Fourier transforms of the corresponding Patterson functions), while the second (cross) term generally leads to smaller additional changes. It should be emphasized that this separation does not correspond to the separation into Bragg and diffuse scattering. Although a further mathematical treatment of this very general expression does not seem to be easy, some qualitative or even semi-quantitative conclusions may be drawn:

(1) If the  $d_i^j$  are coherent with  $l_i$  (*i.e.* the  $\mathbf{m}_i^j$  coincide with lattice points  $\sum m_i \mathbf{a}_i$ ), the convolution with the second term in (4.2.3.38) is meaningless and we obtain sharp (basic) Bragg

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

reflections. This means that domain sizes and distributions cannot be determined from the widths of the Bragg reflections. One has to rely on the second term in this case.

(a) If, in addition, the  $d_i^j$  are strictly periodic (which implies equal sizes  $b_i$ ), superlattice reflections occur that accompany the basic reflections as *satellites*. If the periodicity is *commensurate* with the basic lattice, higher-order satellites may coincide with basic reflections. Hence care must be taken even in the determination of the average structure.

(b) If the periodicity in (a) is not perfect (there are small fluctuations of domain sizes), the satellites will be broadened.

(c) If the distribution of domain sizes is completely random, this will degenerate into a continuous intensity distribution (diffuse streaks). Note, however, that a completely random distribution cannot be realized, since the domains have a *finite* size, *i.e.* there will always be some kind of modulation of the streak.

(2) If the  $d_i^j$  are incoherent, the second terms vanish and the broadening effect of the convolution in the first term becomes effective, *i.e.* the domain size and distribution can be determined directly from the widths of the basic Bragg reflections. This situation may be encountered more frequently in real systems, as usually the fluctuating widths of the domain walls lead to a loss of coherence between different domains of the same type. Nevertheless, one has to be careful if relatively small domain sizes are present, since accidental coincidences may occur that lead to different broadening of different reflections. The problem of coherence effects in these cases is discussed and exemplified by Boysen (2007).

(3) Interferences between domains of *different* kinds may lead to specific extinction rules (governing the distribution of sharp and diffuse reflections). Some examples are given below.

(4) The general reciprocity between direct and reciprocal space means that narrow objects in real space correspond to broad features in reciprocal space and *vice versa*. In particular, for domain walls, which are usually thin in one direction and extended in the other two, we expect a broad feature in one direction (perpendicular to the wall) and narrow ones in the perpendicular directions, *i.e.* streaks. For a single layer (with an ideal interface) this streak will be uniform, *i.e.* without modulations. In order to estimate domain sizes  $W$ , the square of the Fourier transform of a box function (for a special direction  $\mathbf{H}$ )

$$B^2(H) = [\sin(\pi WH)/\pi H]^2 \quad (4.2.3.39)$$

may be used to estimate the half widths of the peaks. Hence measuring the peak broadening in all directions of reciprocal space will give full information about the shape of the domains.

(5a) The situation becomes slightly more complicated when strain effects are present. For small extensions of the strained volume, *e.g.* inside a domain wall, it may be convenient to treat the whole wall as one unit cell, *i.e.* simply calculate the sum over all atoms directly. A strained lattice may generally be written

$$l_s(\mathbf{r}) = \sum_m \delta[\mathbf{r} - \sum m_i \mathbf{a}_i - \mathbf{s}(m)], \quad (4.2.3.40)$$

where the function  $\mathbf{s}(m)$  describes the displacement variation in the different cells. Fourier transformation gives

$$L_s(\mathbf{H}) = \sum_m \exp\{2\pi i \mathbf{H} \cdot \sum m_i \mathbf{a}_i\} \exp\{2\pi i \mathbf{H} \cdot \mathbf{s}(m)\}. \quad (4.2.3.41)$$

For a harmonic (sinusoidal) wave  $\mathbf{s} = \mathbf{z}_0 \sin(2\pi m/M + \varphi)$ , where  $\mathbf{z}_0$ ,  $\varphi$  and  $M$  are the amplitude, the phase and the period of the wave, one gets (Korekawa, 1967)

$$L_s(\mathbf{H}) = \sum_m J_m(2\pi \mathbf{H} \cdot \mathbf{z}_0) \exp\{2\pi i m \varphi\} L(H - m/M), \quad (4.2.3.41a)$$

*i.e.* a set of satellites  $m$  weighted by Bessel functions of order  $m$ . The intensity of the zeroth order (Bragg peak) thus decreases

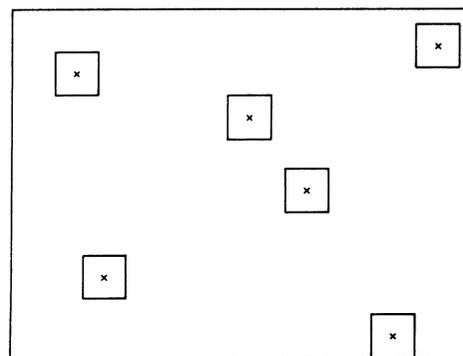


Fig. 4.2.3.1. Model of the two-dimensional distribution of point defects, causing changes in the surroundings.

with  $\mathbf{H}$ , while higher orders become more important. Again, one has to be careful with possible coincidences. This dependence on the scattering vector  $\mathbf{H}$  holds for all other functional forms of  $\mathbf{s}(m)$  as well and is therewith fundamentally different to the behaviour of the size effect, which gives the same contribution to all Bragg reflections, like in the case of density fluctuations. This difference may therefore be used to distinguish between the two effects.

(5b) Again, fluctuations of amplitude and phase lead to a broadening (diffuse tails) of the satellites. A general function  $\mathbf{s}(m)$  may be analysed by expanding it into a Fourier series. For very long wavelengths ( $M$ ) the satellites approach the basic Bragg peaks and cannot be observed easily. The case of a linear strain may be approximated by a sinusoidal modulation with very large wavelength, *i.e.* we will essentially observe a broadening of the Bragg peaks only. Then the strain  $\varepsilon$  may be estimated from the measured width  $\Delta \mathbf{H}$ :

$$\varepsilon = \Delta d/d = \Delta H/H.$$

*Example: Clusters in a periodic lattice (low concentrations)*

The exsolution of clusters of equal sizes is considered. The lattice of the host is undistorted, structure  $F_1$ , and the clusters have the same lattice but a different structure,  $F_2$ . A schematic drawing is shown in Fig. 4.2.3.1. Two different structures are introduced:

$$F_1(\mathbf{r}) = \sum_v \delta(\mathbf{r} - \mathbf{r}_v) * F_v(\mathbf{r}),$$

$$F_2(\mathbf{r}) = \sum_\mu \delta(\mathbf{r} - \mathbf{r}_\mu) * F_\mu(\mathbf{r}).$$

Their Fourier transforms are the structure factors  $F_1(\mathbf{H})$ ,  $F_2(\mathbf{H})$  of the matrix and the exsolved clusters, respectively. The boxes in Fig. 4.2.3.1 indicate the clusters, which may be represented by box functions  $b(\mathbf{r})$  in the simplest case. It should be pointed out, however, that a more complicated shape means nothing other than a replacement of  $b(\mathbf{r})$  by another shape function  $b'(\mathbf{r})$  and its Fourier transform  $B'(\mathbf{H})$ . The distribution of clusters is represented by

$$d(\mathbf{r}) = \sum_{\mathbf{m}} \delta(\mathbf{r} - \mathbf{m}),$$

where  $\mathbf{m}$  refers to the centres of the box functions (the crosses in Fig. 4.2.3.1). The problem is therefore defined by

$$l(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b(\mathbf{r})] * [F_2(\mathbf{r}) - F_1(\mathbf{r})] * d(\mathbf{r}). \quad (4.2.3.42a)$$

The incorrect addition of  $F_1(\mathbf{r})$  to the areas of clusters  $F_2(\mathbf{r})$  is compensated by subtracting the same contribution from the second term in equation (4.2.3.42a). In order to determine the diffuse scattering, the Fourier transformation of (4.2.3.42a) is performed:

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

$$L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}). \quad (4.2.3.42b)$$

The intensity is given by

$$|L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2. \quad (4.2.3.42c)$$

Evaluation of equation (4.2.3.42c) yields three terms (where c.c. means complex conjugate):

- (i)  $|L(\mathbf{H})F_1(\mathbf{H})|^2$
- (ii)  $\{[L(\mathbf{H})F_1(\mathbf{H})][L(\mathbf{H}) * B(\mathbf{H})] \times [F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}) + \text{c.c.}\}$
- (iii)  $\{|[L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2\}$ .

The first two terms represent modulated lattices [multiplication of  $L(\mathbf{H})$  by  $F_1(\mathbf{H})$ ]. Consequently, they cannot contribute to diffuse scattering, which is completely determined by the third term. Fourier transformation of this term gives

$$\begin{aligned} & [l(\mathbf{r})b(\mathbf{r}) * \Delta F(\mathbf{r}) * d(\mathbf{r}) * [l(\mathbf{r})b(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(-\mathbf{r})] \\ &= [l(\mathbf{r})b(\mathbf{r})] * [l(\mathbf{r})b(\mathbf{r}) * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r})] \\ &= [l(\mathbf{r})t(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}), \quad (4.2.3.43a) \end{aligned}$$

where  $l(\mathbf{r}) = l(-\mathbf{r})$ ,  $b(\mathbf{r}) = b(-\mathbf{r})$  and  $\Delta F = F_2 - F_1$ . According to equation (4.2.3.15) and its subsequent discussion, the convolution of the two expressions in square brackets was replaced by  $l(\mathbf{r})t(\mathbf{r})$ , where  $t(\mathbf{r})$  represents the 'pyramid' of  $n$ -fold height discussed above and  $n$  is the number of unit cells within  $b(\mathbf{r})$ .  $d(\mathbf{r}) * d(-\mathbf{r})$  is the Patterson function of the distribution function  $d(\mathbf{r})$ . Its usefulness may be recognized by considering the two possible extreme solutions, namely the random and the strictly periodic distribution.

If no fluctuations of domain sizes are admitted, the minimum distance between two neighbouring domains is equal to the length of the domain in the corresponding direction. This means that the distribution function cannot be completely random. In one dimension, the solution of a random distribution of particles of a given size on a finite length shows that the distribution functions exhibit periodicities that depend on the average free volume of one particle (Zernike & Prins, 1927). Although the problem is more complicated in three dimensions, there should be no fundamental difference in the exact solutions.

On the other hand, it may be shown that the convolution of a pseudo-random distribution may be obtained if the average free volume is large. This is shown in Fig. 4.2.3.2(a) for the particular case of a cluster smaller than one unit cell. A strictly periodic distribution function (a superstructure) may result, however, if the volume of the domain and the average free volume are equal. Obviously, the practical solution for the self-convolution of the distribution function (which is the Patterson function) lies somewhere in between, as shown in Fig. 4.2.3.2(b). If a harmonic periodicity damped by a Gaussian is assumed, this self-convolution of the distribution in real space may be considered to consist of two parts, as shown in Figs. 4.2.3.2(c), (d). Note that the two different solutions result in completely different diffraction patterns:

- (i) The geometrically perfect lattice extends to distances that are large when compared with the correlation length of the distribution function. Then the Patterson function of the distribution function concentrates at the positions of the basic lattice, which is given by multiplication by the lattice  $l(\mathbf{r})$ . The corresponding convolution in reciprocal space gives the same contribution to all Bragg reflections (Fig. 4.2.3.2e).

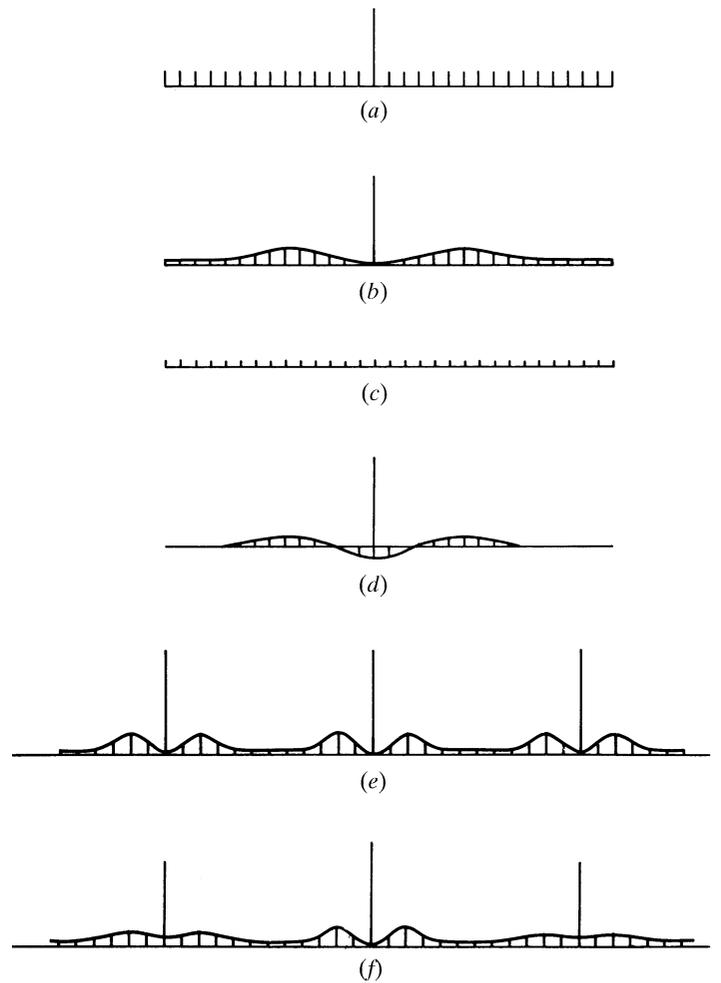


Fig. 4.2.3.2. One-dimensional Patterson functions of various point-defect distributions: (a) random distribution; (b) influence of finite volume of defects on the distribution function; (c), (d) decomposition of (b) into a periodic (c) and a convergent (d) part; (e) Fourier transform of (c) + (d); (f) changes of (e) if the centres of the defects show major deviations from the origins of the lattice.

- (ii) There is no perfect lattice geometry. In this case, a continuous Patterson function results. Fourier transformation yields an influence that is now restricted primarily to the reflection 000, *i.e.* to the low-angle diffraction range.

Figs. 4.2.3.2(e), (f) show the different diffraction patterns of the diffuse scattering that is concentrated around the Bragg maxima. Although the discussion of the diffuse scattering was restricted to the case of identical domains, the introduction of a distribution of domain sizes does not influence the diffraction pattern essentially, as long as the fluctuation of sizes is small compared with the average volume of domain sizes and no strong correlation exists between domains of any size (a size-independent random distribution).

A complete qualitative discussion of the diffraction pattern may be carried out by investigating the Fourier transform of (4.2.3.43a):

$$[L(\mathbf{H}) * T(\mathbf{H})]|\Delta F(\mathbf{H})|^2|D(\mathbf{H})|^2. \quad (4.2.3.43b)$$

The first factor in (4.2.3.43b) describes the particle-size effect of a domain containing the influence of a surrounding strain field and the new structure of the domains precipitated from the bulk.  $D(\mathbf{H})$  has its characteristic variation near the Bragg peaks (Figs. 4.2.3.2e,f) and is less important in between. For domain structure determination, intensities near the Bragg peaks should be avoided. Note that equation (4.2.3.43b) may be used for measurements using anomalous scattering in both the centric and the acentric case.

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

*Solution of the diffraction problem.* In equation (4.2.3.43b)  $\Delta F(\mathbf{H})$  is replaced by its average,

$$\langle \Delta F(\mathbf{H}) \rangle = \sum_{\mu} p_{\mu} \Delta F_{\mu}(\mathbf{H}),$$

where  $p_{\mu}$  represents the *a priori* probability of a domain of type  $\mu$ . This replacement becomes increasingly important if small clusters (domains) have to be considered. Applications of the formulae to Guinier–Preston zones are given by Guinier (1942) and Gerold (1954); a similar application to clusters of vacancies in spinels with an excess of  $\text{Al}_2\text{O}_3$  was outlined by Jagodzinski & Haefner (1967).

Although refinement procedures are possible in principle, the number of parameters entering the diffraction problem becomes increasingly large if more clusters or domains (of different sizes) have to be introduced. Another difficulty results from the large number of diffraction data which must be collected to perform a reliable structure determination. There is no need to calculate the first two terms in equation (4.2.3.42c) which contribute to the sharp Bragg peaks only, because their intensity is simply described by the averaged structure factor  $|\langle F(\mathbf{H}) \rangle|^2$ . These terms may therefore be replaced by

$$|L(\mathbf{H})|^2 |\langle F(\mathbf{H}) \rangle|^2$$

with

$$|\langle F(\mathbf{H}) \rangle|^2 = \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2, \quad (4.2.3.43c)$$

where  $p_{\mu}$  is the *a priori* probability of the structure factor  $F_{\mu}(\mathbf{H})$ . It should be emphasized here that (4.2.3.43c) is independent of the distribution function  $d(\mathbf{r})$  or its Fourier transform  $D(\mathbf{H})$ .

While a number of solutions to the diffraction problem may be found in the literature for one-dimensional (1D) disorder (1D distribution functions) (see, e.g., Jagodzinski, 1949*a,b,c*; Cowley, 1976*a,b*; Adlhart, 1981; Pflanz & Moritz, 1992), these become increasingly more complicated with increasing dimensionality. These types are therefore discussed separately in the following.

##### 4.2.3.5.4. One-dimensional disorder

This lamellar (1D) type of disorder is common in many crystals for energetic reasons. For example, most of the important rock-forming minerals exhibit such disorder behaviour. Therefore we give some extended introduction to this field. To illustrate the application of the formalism outlined above, we start with a simple example of domains of an identical structure  $\rho(\mathbf{r})$  displaced relative to each other by an arbitrary fault vector  $\Delta$  (Boysen *et al.*, 1991). If  $t(\mathbf{r})$  describes the regions of one domain, then  $1 - t(\mathbf{r})$  describes those of the displaced domains and the complete structure may be written

$$t(\mathbf{r})[\rho(\mathbf{r})] + [1 - t(\mathbf{r})][\rho(\mathbf{r} - \Delta)].$$

Introducing  $t'(\mathbf{r}) = 2t(\mathbf{r}) - 1$ , this may be rewritten as

$$[l(\mathbf{r}) + l(\mathbf{r} - \Delta)] * \rho(\mathbf{r}) / 2 = t'(\mathbf{r}) \{ [l(\mathbf{r}) - l(\mathbf{r} - \Delta)] * \rho(\mathbf{r}) \} / 2.$$

Fourier transformation yields

$$L(\mathbf{H}) [1 + \exp\{2\pi i \Delta \cdot \mathbf{r}\}] F(\mathbf{H}) / 2 \\ + T'(\mathbf{H}) * L(\mathbf{H}) [1 - \exp\{2\pi i \Delta \cdot \mathbf{r}\}] F(\mathbf{H}) / 2.$$

The first term describes sharp reflections due to the multiplication with the lattice function  $L(\mathbf{H})$ , while the second term gives diffuse reflections due to the convolution with  $T'(\mathbf{H})$ . The corresponding intensities are

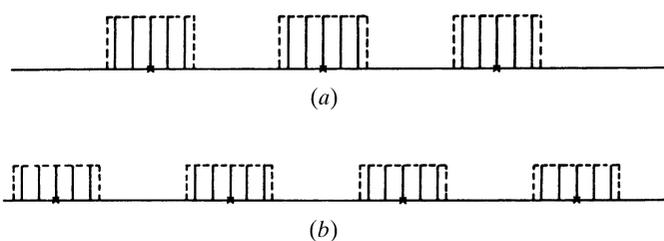


Fig. 4.2.3.3. Periodic array of domains consisting of two different atoms, represented by different heights. (a) Distribution of domain type 1, (b) distribution of domain type 2.

$$I_S \propto 1 + \cos(2\pi \Delta \cdot \mathbf{H}) \text{ and } I_D \propto 1 - \cos(2\pi \Delta \cdot \mathbf{H}).$$

In the general case, all reflections consist of a superposition of sharp and diffuse intensities. Note that the well known separation of sharp and diffuse intensities for antiphase domains is obtained if  $\Delta$  equals  $\frac{1}{2}$  times a lattice vector.

##### (1) Periodic distribution of lamellar domains

Here  $d(\mathbf{r})$  is one-dimensional and can easily be calculated: a periodic array of two types of lamellae having the same basic lattice  $l(\mathbf{r})$  but different structures is shown in Fig. 4.2.3.3. The sizes of the two types of lamellae may be different. The structure of the first domain type is given by a convolution with  $F_1(\mathbf{r})$  (Fig. 4.2.3.3a) and that of the second domain type by  $F_2(\mathbf{r})$  (Fig. 4.2.3.3b). Introducing  $\langle F(\mathbf{r}) \rangle$  and  $\Delta F(\mathbf{r})$ , the structure in real space is described by

$$[l(\mathbf{r})b_1(\mathbf{r})] * d(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) * F_2(\mathbf{r}) \\ = \{ [l(\mathbf{r})b_1(\mathbf{r}) + l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) \} * \langle F(\mathbf{r}) \rangle \\ + [l(\mathbf{r})b_1(\mathbf{r}) - l(\mathbf{r})b_2(\mathbf{r})] * d(\mathbf{r}) * \Delta F(\mathbf{r}). \quad (4.2.3.44a)$$

Obviously, the first term in curly brackets in equation (4.2.3.44a) is no more than  $l(\mathbf{r})$  itself and  $d(\mathbf{r})$  is strictly periodic.  $b_1(\mathbf{r})$  and  $b_2(\mathbf{r})$  are box functions, mutually displaced by  $\pm(n_1 + n_2)/2$  unit cells in the stacking direction [ $n_1, n_2$  are the numbers of cells covered by  $b_1(\mathbf{r})$  and  $b_2(\mathbf{r})$ , respectively].

Fourier transformation of equation (4.2.3.44a) yields

$$L(\mathbf{H}) \langle F(\mathbf{H}) \rangle + \{ L(\mathbf{H}) * [B_1(\mathbf{H}) - B_2(\mathbf{H})] \} D(\mathbf{H}) \Delta F(\mathbf{H}). \quad (4.2.3.44b)$$

The first term in equation (4.2.3.44b) gives the normal sharp reflections of the average structure, while the second describes superlattice reflections [sublattice  $L_s(\mathbf{H}) = D(\mathbf{H})$  in reciprocal space], multiplied by  $\Delta F(\mathbf{H})$  and another 'structure factor' generated by the convolution of the reciprocal lattice  $L(\mathbf{h})$  with  $[B_1(\mathbf{H}) - B_2(\mathbf{H})]$  (cf. Fig. 4.2.3.3). Since the centres of  $b_1(\mathbf{r})$  and  $b_2(\mathbf{r})$  are mutually displaced, the expression in square brackets includes extinctions if  $b_1(\mathbf{r})$  and  $b_2(\mathbf{r})$  represent boxes equal in size. These extinctions are discussed below. It should be pointed out that  $L_s(\mathbf{H})$  and its Fourier transform  $l_s(\mathbf{r})$  are commensurate with the basic lattice as long as no change of the translation vector at the interface of the lamellae occurs. Obviously,  $L_s(\mathbf{H})$  becomes incommensurate in the general case of a slightly distorted interface. Considerations of this kind play an important role in the discussion of modulated structures.

No assumption has been made so far about the position of the interface. This point is meaningless only in the case of a strictly periodic array of domains (with no diffuse scattering). Therefore it seems to be convenient to introduce two basis vectors parallel to the interface in real space, which demand a new reciprocal vector perpendicular to them defined by  $(\mathbf{a}' \times \mathbf{b}')/V'$ , where  $\mathbf{a}'$ ,  $\mathbf{b}'$  are the new basis vectors and  $V'$  is the volume of the supercell. As long as the new basis vectors are commensurate with the original lattice, the direction of the new reciprocal vector  $\mathbf{c}^*$ , perpendicular to  $\mathbf{a}'$ ,  $\mathbf{b}'$ , passes through the Bragg points of the original reciprocal lattice and the reciprocal lattice of the superlattice

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

remains commensurate as long as  $V'$  is a multiple of  $V$  ( $V' = mV$ ,  $m = \text{integer}$ ). Since the direction of  $\mathbf{c}$  is arbitrary to some extent, there is no clear rule about the assignment of superlattice reflections to the original Bragg peaks. This problem becomes very important if extinction rules of the basic lattice and the superlattice have to be described together.

### Example

We consider a b.c.c. structure with two kinds of atoms (1, 2) with a strong tendency towards superstructure formation (CsCl-type ordering). According to equations (4.2.3.43b,c) and (4.2.3.44b), in the case of negligible short-range order we obtain the following expressions for sharp and diffuse scattering (where  $c = \text{concentration}$ ):

$$I_S = |cf_1(\mathbf{H}) + (1-c)f_2(\mathbf{H})|^2 \quad \text{for } h+k+l = 2n,$$

$$I_D = c(1-c)|f_1(\mathbf{H}) - f_2(\mathbf{H})|^2 \quad \text{elsewhere.}$$

With increasing short-range order the sharp reflections remain essentially unaffected, while the diffuse ones concentrate into diffuse maxima at  $\mathbf{h}$  with  $h+k+l = 2n+1$ . This process is treated more extensively below. As long as the domains exhibit no clear interface, it is useful to describe the ordering process with the two possible cell occupations of a pair of different atoms; then contributions of equal pairs may be neglected with increasing short-range order. Now the two configurations 1, 2 and 2, 1 may be given with the aid of the translation  $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$ . Hence the two structure factors are

$$F_1 \text{ and } F_2 = F_1 \exp\{\pi i(h+k+l)\}.$$

Since the two structure factors occur with the same probability, the equations for sharp and diffuse reflections become

$$I_S = \frac{1}{4}|F_1(\mathbf{H})|^2 [1 + \exp\{\pi i(h+k+l)\}]^2,$$

$$I_D = \frac{1}{4}|F_1(\mathbf{H})|^2 [1 - \exp\{\pi i(h+k+l)\}]^2.$$

It is well recognized that no sharp reflections may occur for  $h+k+l = 2n+1$ , and the same holds for the diffuse scattering if  $h+k+l = 2n$ . This extinction rule for diffuse scattering is due to suppression of the contributions of equal pairs. The situation becomes different for lamellar structures. Let us first consider the case of lamellae parallel to (100). The ordered structure is formed by an alternating sequence of monoatomic layers consisting of atoms of types 1 or 2. Hence the interface between two neighbouring domains is a pair of equal layers 1, 1 or 2, 2, which are not equivalent. Each interface of type 1 (2) may be described by an inserted layer of type 1 (2) and the chemical composition differs from 1:1 if one type of interface is preferred. Since the contribution of equal pairs has been neglected in deriving the extinction rule of diffuse scattering (see above), this rule is no longer valid. Because of the lamellar structure the diffuse intensity is concentrated into streaks parallel to (00 $l$ ). Starting from the diffuse maximum (010), the diffuse streak passes over the sharp reflection 011 to the next diffuse one 012 *etc.*, and the extinction rule is violated as long as one of the two interfaces is predominant. Therefore, the position of the interface determines the extinction rule in this orientation.

A completely different behaviour is observed for lamellae parallel to (110). This structure is described by a sequence of equal layers containing atoms 1 and 2. The interface between two domains (exchange of the two different atoms) is now nothing other than the displacement parallel to the layer of the original one in the ordered sequence. Calculation of the two structure factors would involve displacements  $\pm \frac{1}{2}(\mathbf{a} - \mathbf{b})$ . Starting from the diffuse reflection 001, the diffuse streak parallel to (HH0) passes through (111), (221), (331), *...*; *i.e.* through diffuse reflections only. On the other hand, rows

(HH2) going through (002), (112), (222), *...* do not show any diffuse scattering. Hence we have a new extinction rule for diffuse scattering originating from the orientation of interfaces. This fact is rather important in structure determination. For various reasons, lamellar interfaces show a strong tendency towards a periodic arrangement. In diffraction the diffuse streak then concentrates into quite sharp superstructure reflections. These are not observed on those rows of the reciprocal lattice that are free from diffuse scattering. The same extinction law is not valid in the case of the (100) orientation of the interfaces. Summarizing, we may state that three types of extinction rules have to be considered:

- (a) Normal extinctions for the average structure.
- (b) Extinction of the difference structure factors for diffuse scattering.
- (c) Extinctions caused by the ordering process itself.

(2) *Lamellar system with two different structures, where  $\langle F(\mathbf{H}) \rangle$  and  $\Delta F(\mathbf{H})$  do not obey any systematic extinction law*

The convolution of the second term in equation (4.2.3.44b) (*cf.* Fig. 4.2.3.3) may be represented by a convolution of the Fourier transform of a box function  $B_1(\mathbf{H})$  with the reciprocal superlattice. Since  $B_1(\mathbf{H})$  is given by  $\sin(\pi m_s H)/(\pi H)$ , where  $m_s$  is the number of cells in the supercell, the reader might believe that the result of the convolution may easily be determined quantitatively: this assumption is not correct because of the slow convergence of  $B_1(\mathbf{H})$ . The systematic coincidences of the maxima, or minima, of  $B_1(\mathbf{H})$  with the points of the superlattice in the commensurate case cause considerable changes in intensities, especially in the case of a small domain thickness. For this reason, an accurate calculation of the amplitudes of the satellites is necessary (Jagodzinski & Penzkofer, 1981):

- (a) Bragg peaks of the basic lattice

$$I \simeq |\langle F(\mathbf{H}) \rangle|^2; \quad (4.2.3.45a)$$

- (b) satellites:  $\nu = 2n$  ( $n = \text{integer except } 0$ )

$$I \simeq |2 \sin \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2; \quad (4.2.3.45b)$$

- (c) satellites:  $\nu = 2n + 1$

$$I \simeq |2 \cos \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2. \quad (4.2.3.45c)$$

Here  $\nu$  is the order of the satellites,  $C = \frac{1}{2}(N_1 - N_2)/(N_1 + N_2)$ , and  $N_1$  and  $N_2$  are the number of cells within  $b_1(\mathbf{r})$  and  $b_2(\mathbf{r})$ , respectively.

Obviously, there is again a systematic extinction rule for even satellites if  $N_1 = N_2$ .

Equation (4.2.3.45b) indicates an increasing intensity of first even-order satellites with increasing  $C$ . Intensities of first even and odd orders become nearly equal if  $N_2 \simeq \frac{1}{2}N_1$ . Smaller values of  $N_2$  result in a decrease of intensities of both even and odd orders (no satellites occur if  $N_2 = 0$ ). The denominators in equations (4.2.3.45b,c) indicate a decrease in intensity with increasing order of the satellites. The quantitative behaviour of the intensities needs a more detailed discussion of the numerator in equations (4.2.3.45b,c) with increasing order of the satellites. Obviously, there are two kinds of extinction rules to be taken into account: systematic absences for the various orders of satellites, and the usual extinctions for  $\langle F(\mathbf{H}) \rangle$  and  $\Delta F(\mathbf{H})$ . Each has to be considered separately in order to arrive at reliable conclusions. This different behaviour of the superlattice reflections (satellites) and that of the basic lattice may be represented by a multi-dimensional group-theoretical representation, as has been shown by de Wolff (1974), Janner & Janssen (1980a,b), de Wolff *et al.* (1981) and others.

- (3) *Nonperiodic system of lamellar domains*

Following the discussion of equations (4.2.3.43), one may conclude that the fluctuations of domain sizes cause a broadening of satellites if the periodic distribution function has to be

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

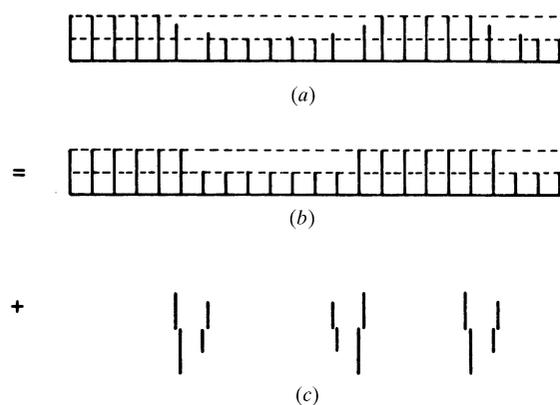


Fig. 4.2.3.4. Influence of distortions at the boundary of domains and separation into two parts; for discussion see text.

replaced by a statistical one. In this case, the broadening effect increases with the order of the satellites. The intensities, however, are completely determined by the distribution function and can be estimated by calculating the intensities of the perfectly ordered array, as approximated by the distribution function.

A careful check of  $\langle F(\mathbf{H}) \rangle$  and  $\Delta F(\mathbf{H})$  in equations (4.2.3.45) shows that the position of the interface plays an important role in the intensities of the satellites. Since this position determines the origin of the unit cells in the sublattice, we have to choose this origin for the calculation of  $F(\mathbf{H})$  and  $\Delta F(\mathbf{H})$ . This involves phase factors which are meaningless for integral values of  $\mathbf{H}$  (i) if the average  $\langle F(\mathbf{H}) \rangle$  refers to different structures with arbitrary origin or (ii), which is important for practical cases, where no change occurs in the origin of related structures for neighbouring domains that are bound to an origin by general convention (e.g. a centre of symmetry). This statement is no longer true for non-integral values of  $\mathbf{H}$ , which are needed for the calculation of intensities of satellites. The intensities of satellites become different for different positions of the interface even in the absence of a relative displacement between neighbouring domains with respect to an origin by convention. This statement may be extended to nonperiodic distribution functions. Consequently, one may conclude that the study of diffuse scattering yields information on the interfacial scattering. For slightly different structures at the interface two cases are important:

(i) the two structures are related by symmetry (e.g. by a twin law); and

(ii) the difference between the two structures cannot be described by a symmetry operation.

In structures based on the same sublattice, the first case seems to be more important, because two different structures with the same sublattice are improbable. In the first case there is an identical sublattice if the symmetry operation in question does not influence the plane of intergrowth, e.g. a mirror plane should coincide with the plane of intergrowth. Since we have two inequivalent mirror planes in any sublattice, there are two such planes. It is assumed that no more than one unit cell of both domains at the interface has a slightly different structure without any change of geometry of the unit cell, and the number of unit cells is equal because of the equivalence of both domain structures (twins). Fig. 4.2.3.4(a) shows a picture of this model; Figs. 4.2.3.4(b), (c) explain that this structure may be described by two contributions:

(i) The first term is already given by equation (4.2.3.45) for  $N_1 = N_2$ , consequently only odd orders of satellites are observed.

(ii) The second term may be described by a superlattice containing  $2N_1$  cells with an alternating arrangement of interfaces, correlated by the relevant plane of symmetry.

In real space, the second term may be constructed by convolution of the one-dimensional superlattice with two difference

structures displaced by  $\mp N_1/2$  units of the sublattice; its Fourier transformation yields

$$L_s(\mathbf{H})[\Delta F_i(\mathbf{H}) \exp\{2\pi i N_1 H/2\} + \Delta F'_i(\mathbf{H}) \exp\{-2\pi i N_1 H/2\}], \quad (4.2.3.46)$$

where  $\Delta F_i, \Delta F'_i$  correspond to the Fourier transforms of the contributions shown in Fig. 4.2.3.4(c). Since  $H = \nu/N_1$ , there are alternating contributions to the  $\nu$ th satellite which may be calculated more accurately by taking into account the symmetry operations. The important difference between equations (4.2.3.45) and (4.2.3.46) is the missing decrease in intensity with increasing order of the satellites. Consequently, one may conclude that the interface contributes to low- and high-order satellites as well, but its influence prevails for high-order satellites. Similar considerations may be made for two- and three-dimensional distributions of domains. A great variety of extinction rules may be found depending on the type of order approximated by the distribution under investigation.

(4) *Two kinds of lamellar domains with variable size distribution*

The preceding discussion of the diffuse scattering from domains is obviously restricted to relatively small fluctuations of domain sizes. This is specifically valid if the most probable domain size does not differ markedly from the average size. This condition is violated in the case of order-disorder phenomena. It may happen that the smallest ordered area is the most probable one, although the average is considerably larger. This may be shown for a lamellar structure of two types of layers correlated by a (conditional) pair probability  $p_{\mu\mu'}(\mathbf{1})$ . As shown below, a pair at distance  $\mathbf{m}$  occurs with the probability  $p_{\mu} p_{\mu\mu'}(\mathbf{m})$ , which may be derived from the pair probability of nearest neighbours  $p_{\mu} p_{\mu\mu'}(\mathbf{1})$ . (In fact only one component of vector  $\mathbf{m}$  is relevant in this context.) The problem will be restricted to two kinds of layers ( $\mu, \mu' = 1, 2$ ). Furthermore, it will be symmetric in the sense that the pair probabilities obey the following rules:

$$p_{11}(\mathbf{m}) = p_{22}(\mathbf{m}), \quad p_{12}(\mathbf{m}) = p_{21}(\mathbf{m}). \quad (4.2.3.47)$$

It may be derived from equation (4.2.3.47) that the *a priori* probabilities  $p_{\mu}$  of a single layer are  $\frac{1}{2}$  and

$$p_{11}(\mathbf{0}) = p_{22}(\mathbf{0}) = 1, \quad p_{12}(\mathbf{0}) = p_{21}(\mathbf{0}) = 0.$$

With these definitions and the general relation

$$p_{11}(\mathbf{m}) + p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) + p_{21}(\mathbf{m}) = 1,$$

the *a priori* probability of a domain containing  $m$  layers of type 1 may be calculated with the aid of  $p_{11}(\mathbf{1})$  [ $0 \leq p_{11}(\mathbf{1}) \leq 1$ ]:

$$p_{\mu} = \frac{1}{2} p_{11}(\mathbf{1})^{m-1} [1 - p_{11}(\mathbf{1})]. \quad (4.2.3.48)$$

Hence the most probable size of domains is a single layer, because a similar relation holds for layers of type 2. Since the average thickness of the domains is strongly dependent on  $p_{11}(\mathbf{1})$  [infinite for  $p_{11}(\mathbf{1}) = 1$  and one layer for  $p_{11}(\mathbf{1}) = 0$ ], it may become very large in the latter case. Consequently, there are extremely large fluctuations if  $p_{11}(\mathbf{1})$  is small but different from zero.

It may be concluded from equation (4.2.3.48) that the function  $p_{11}(\mathbf{m})$  decreases monotonically with increasing  $\mathbf{m}$ , approaching  $\frac{1}{2}$  with  $\mathbf{m} \rightarrow \infty$ . It is apparent that this cannot be true for a finite crystal if  $p_{11}(\mathbf{m})$  is unity (a structure of two types of domains) or zero (a superstructure of alternating layers). In either case, the crystal should consist of a single domain of type 1 or 2, or one of the possible superstructures 1212 ... , 2121 ... , respectively. Hence one has to differentiate between long-range order, where two equivalent solutions have to be considered, and short-range order, where  $p_{11}(\mathbf{m})$  approaches the *a priori* probability  $\frac{1}{2}$  for large  $m$ . This behaviour of  $p_{11}(\mathbf{m})$  and  $p_{12}(\mathbf{m})$ , which may also be

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

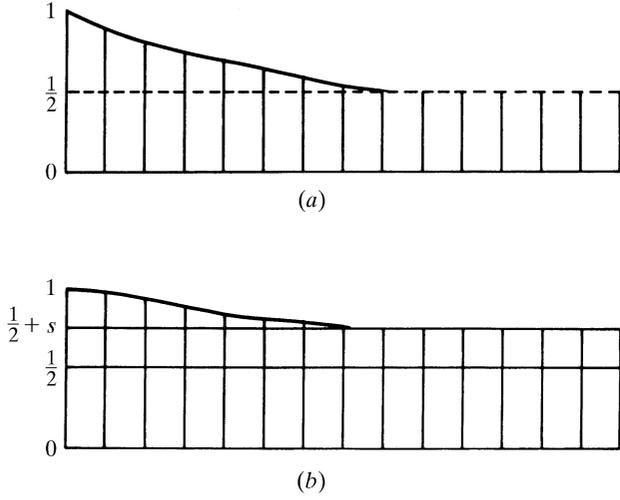


Fig. 4.2.3.5. Behaviour of  $p_{11}(\mathbf{m})$  and  $p_{12}(\mathbf{m})$  in mixed crystals (unmixing): (a) upper curve: short-range order only; (b) lower curve: long-range order.

expressed by equivalent correlation functions, is shown in Figs. 4.2.3.5(a) (short-range order) and 4.2.3.5(b) (long-range order, quantified by the parameter  $s$ ).  $p_{11}(\mathbf{m})$  approaches  $\frac{1}{2} + s$  for large  $m$  with  $s = 0$  in the case of short-range order, while  $p_{12}(\mathbf{m})$  becomes  $\frac{1}{2} - s$ . Obviously, a strict correlation between  $p_{11}(\mathbf{1})$  and  $s$  exists, and this has to be calculated. For a qualitative interpretation of the diffraction pictures this correlation may be derived from the diffraction pattern itself. The  $p_{\mu\mu'}(\mathbf{m})$  are separable into a strictly periodic and a monotonically decreasing term approaching zero in both cases. This behaviour is shown in Figs. 4.2.3.6(a), (b). The periodic term contributes to sharp Bragg scattering. In the case of short-range order, the symmetry relations given in equation (4.2.3.47) are valid. The convolution in real space yields with factors  $t(\mathbf{r})$  (equation 4.2.3.43a):

$$\begin{aligned} & \frac{1}{2}t(\mathbf{r}) \left[ \sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{11}(\mathbf{m}) \right] * F_1(\mathbf{r}) * F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r}) \left[ \sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{12}(\mathbf{m}) \right] * F_1(\mathbf{r}) * F_2(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r}) \left[ \sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{21}(\mathbf{m}) \right] * F_2(\mathbf{r}) * F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r}) \left[ \sum_{\mathbf{m}} \delta(\mathbf{r} + \mathbf{m}) p'_{22}(\mathbf{m}) \right] * F_2(\mathbf{r}) * F_2(-\mathbf{r}), \end{aligned}$$

where  $p'_{\mu\mu'}(\mathbf{m})$  are factors attached to the  $\delta$  functions:

$$\begin{aligned} p'_{11}(\mathbf{m}) &= p_{11}(\mathbf{m}) - \frac{1}{2} = p'_{22}(\mathbf{m}), \\ p'_{12}(\mathbf{m}) &= p'_{21}(\mathbf{m}) = -p'_{11}(\mathbf{m}). \end{aligned}$$

The positive sign of  $\mathbf{m}$  in the  $\delta$  functions results from the convolution with the inverted lattice (*cf.* Patterson, 1959). Fourier transformation of the four terms given above yields the four corresponding expressions with  $\mu, \mu' = 1, 2$ :

$$\frac{1}{2} \left[ T(\mathbf{H}) * \sum_{\mathbf{m}} p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{m}\} \right] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.49a)$$

Now the summation over  $\mathbf{m}$  may be replaced by an integral if the factor  $l(\mathbf{m})$  is added to  $p'_{\mu\mu'}(\mathbf{m})$ , which may then be considered as the smoothest continuous curve passing through the relevant integer values of  $\mathbf{m}$ :

$$\sum \rightarrow \int l(\mathbf{m}) p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{m}\} d\mathbf{m}.$$

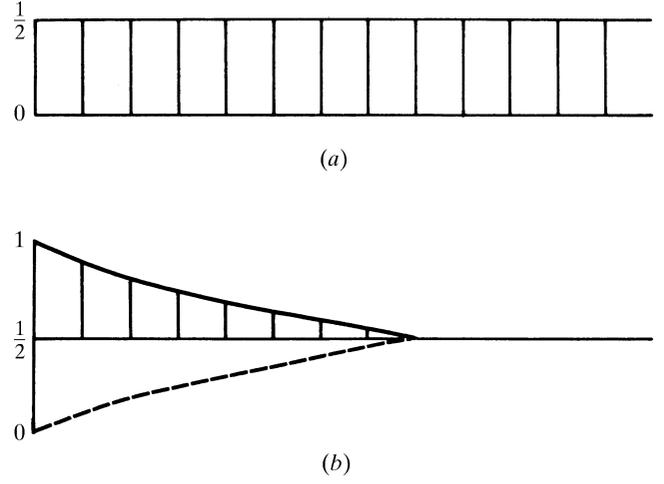


Fig. 4.2.3.6. Decomposition of Fig. 4.2.3.5(a) into (a) a periodic and (b) a rapidly convergent part.

Since both  $l(\mathbf{m})$  and  $p'_{\mu\mu'}(\mathbf{m})$  are symmetric in our special case, we obtain

$$\sum = L(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H}).$$

Insertion of the sum in equation (4.2.3.49a) results in

$$\frac{1}{2} [L(\mathbf{H}) * T(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H})] F_{\mu}(\mathbf{H}) F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.49b)$$

Using all symmetry relations for  $p'_{\mu\mu'}(\mathbf{m})$  and  $P'_{\mu\mu'}(\mathbf{H})$ , respectively, we obtain for the diffuse scattering after summing over  $\mu, \mu'$

$$I_D \simeq [L(\mathbf{H}) * T(\mathbf{H}) * P'_{11}(\mathbf{H})] |\Delta F(\mathbf{H})|^2 \quad (4.2.3.50)$$

with  $\Delta F(\mathbf{H}) = \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]$ .

It should be borne in mind that  $P'_{11}(\mathbf{H})$  decreases rapidly if  $p'_{11}(\mathbf{r})$  decreases slowly and *vice versa*. It is interesting to compare the different results from equations (4.2.3.43b) and (4.2.3.50). Equation (4.2.3.50) indicates diffuse maxima at the positions of the sharp Bragg peaks, while the multiplication by  $D(\mathbf{H})$  causes satellite reflections in the neighbourhood of Bragg maxima. Both equations contain the factor  $|\Delta F(\mathbf{H})|^2$ , indicating the same influence of the two structures. More complicated formulae may be derived for several cell occupations. In principle, a result similar to equation (4.2.3.50) will be obtained, but more interdependent correlation functions  $p_{\mu\mu'}(\mathbf{r})$  have to be introduced. Consequently, the behaviour of diffuse intensities becomes more differentiated in so far as all  $p_{\mu\mu'}(\mathbf{r})$  are now correlated with the corresponding  $\Delta F_{\mu}(\mathbf{r}), \Delta F_{\mu'}(-\mathbf{r})$ . Hence the method of correlation functions becomes increasingly ineffective with an increasing number of correlation functions. Here the cluster method seems to be more convenient and is discussed below.

(5) *Lamellar domains with long-range order: tendency to exsolution*

The Patterson function of a disordered crystal exhibiting long-range order is shown in Fig. 4.2.3.5(b). Now  $p_{11}(\infty)$  converges against  $\frac{1}{2} + s$  and the *a priori* probability changes correspondingly. Since  $p_{12}(\infty)$  becomes  $\frac{1}{2} - s$ , the symmetry relation given in equation (4.2.3.47) is violated:  $p_{11}(\mathbf{r}) \neq p_{22}(\mathbf{r})$  for a finite crystal; it is evident that another crystal shows long-range order with the inverted correlation function,  $p_{22}(\infty) = \frac{1}{2} + s$ ,  $p_{21}(\infty) = \frac{1}{2} - s$ , such that the symmetry  $p_{11}(\mathbf{r}) = p_{22}(\mathbf{r})$  is now valid for an assembly of finite crystals only. According to Fig. 4.2.3.5(b), there is a change in the intensities of the Bragg peaks.

$$\begin{aligned} I_1 &\simeq |(\frac{1}{2} + s)F_1(\mathbf{H}) + (\frac{1}{2} - s)F_2(\mathbf{H})|^2, \\ I_2 &\simeq |(\frac{1}{2} + s)F_2(\mathbf{H}) + (\frac{1}{2} - s)F_1(\mathbf{H})|^2, \end{aligned} \quad (4.2.3.51)$$

#### 4. DIFFUSE SCATTERING AND RELATED TOPICS

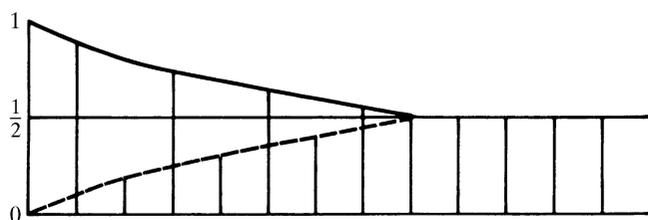


Fig. 4.2.3.7. The same distribution (cf. Fig. 4.2.3.5) in the case of superstructure formation.

where  $I_1, I_2$  represent the two solutions discussed for the assembly of crystals and have to be added with the probability  $\frac{1}{2}$ ; the intensities of sharp reflections become

$$I = (I_1 + I_2)/2. \quad (4.2.3.52)$$

Introducing equation (4.2.3.51) into (4.2.3.52), we obtain

$$I \simeq \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 + s^2|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2. \quad (4.2.3.53a)$$

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

$$I \simeq \frac{1}{2}[|F_1(\mathbf{H})|^2 + |F_2(\mathbf{H})|^2]. \quad (4.2.3.53b)$$

This result reveals some difficulties for the 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 that describe the remaining nonperiodic 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:

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

With the definitions introduced above it is found that

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

The diffuse scattering is given by

$$I_{1D}(\mathbf{H}) = (\frac{1}{4} - s^2)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2 [P'_{11}(\mathbf{H}) * L(\mathbf{H})]. \quad (4.2.3.54)$$

Since equation (4.2.3.54) is symmetrical with respect to an interchange of  $F_1$  and  $F_2$ , the same result is obtained for  $I_{2D}$ . 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  $P'_{11}(\mathbf{H})$ , hence

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

since  $p_{11}(\mathbf{0}) = 1$ .

(6) *Lamellar domains with long-range order: tendency to superorder*

So far it has been tacitly assumed that the crystal shows a preference for equal neighbours. If there is a reversed tendency (*i.e.* 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 undisplaced origin and the displaced one. Fourier transformation of the new functions yields the following very similar results:

*Sharp Bragg reflections*

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

$$I_S = |\frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]|^2. \quad (4.2.3.55a)$$

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

$$I_S = s^2 |\frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]|^2. \quad (4.2.3.55b)$$

*Diffuse reflections*

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

$$I_D = (\frac{1}{4} - s^2) |\frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]|^2. \quad (4.2.3.55c)$$

In contrast to (5), this is the better situation for the 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 possible presence of 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.

##### 4.2.3.5.5. Two-dimensional disorder

The subject of two-dimensional disorder refers to predominantly one-dimensional structural elements, *e.g.* extended macromolecules and chain- or column-like structural units. A short introduction to this subject and some examples taken from inorganic structures are given in Section 4.2.5.3. Most important in this context, however, would be a treatment of disorder diffuse scattering of polymer/fibre structures. These are subjects in their own right and are treated in Chapter 4.5 of this volume and in Chapter 19.5 of Volume F.

##### 4.2.3.5.6. Three-dimensional disorder

The solution of three-dimensional disorder problems is generally more demanding, although it may start with the formulation given above. Various algorithms have been developed to tackle these problems at least approximately, most of them restricted to particular models. Both real-space (cluster) and reciprocal-space (fluctuation wave) methods are employed and will be briefly addressed in Section 4.2.5.4. The more recently

## 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.