

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

(2) Lattices

Lattices in real and reciprocal space may be described by δ functions

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

and

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

where \mathbf{n} , \mathbf{h} represent the components of the displacement 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 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, non-periodic 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 δ function. This fact may easily be understood by applying the law of displacement given in equation (4.2.3.7).

(3) Box functions

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

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

α , β , γ 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 is needed for the calculation of intensities:

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

$t(\mathbf{r})$ 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.

(4) 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 δ 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 function (or self- or auto-

convolution) 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 seems to be 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:

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

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 into the positive direction and an inversion at the displaced origin before multiplication and subsequent integration. On comparing both 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 of

$$a(\mathbf{r} - \mathbf{m}) * b(\mathbf{r} - \mathbf{m}') = \int_{\mathbf{r}'} a(\mathbf{r}' - \mathbf{m}) b(\mathbf{r} - \mathbf{m}' - \mathbf{r}') d\mathbf{r}' \\ = \int_{\mathbf{r}''} a(\mathbf{r}'') b(\mathbf{r} - \mathbf{m}' - \mathbf{m} - \mathbf{r}'') d\mathbf{r}'' \quad (4.2.3.18)$$

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).

4.2.3.1.2. Applications

(1) Clusters in a periodic lattice (low concentrations)

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

$$F_1(\mathbf{r}) = \sum_{\nu} \delta(\mathbf{r} - \mathbf{r}_{\nu}) * F_{\nu}(\mathbf{r}) \\ F_2(\mathbf{r}) = \sum_{\mu} \delta(\mathbf{r} - \mathbf{r}_{\mu}) * F_{\mu}(\mathbf{r}).$$

Their Fourier transforms are the structure factors $F_1(\mathbf{H})$, $F_2(\mathbf{H})$. The bold lines 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

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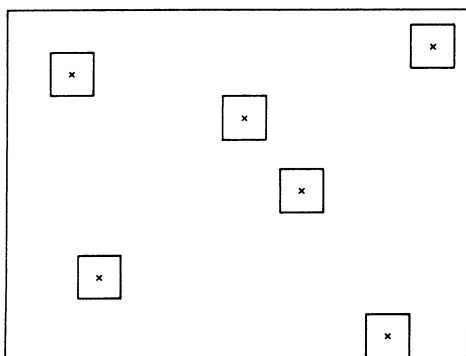


Fig. 4.2.3.1. Model of the two-dimensional distribution of point defects, causing changes in the surroundings.

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

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

$$l(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b(\mathbf{r})] * [F_2(\mathbf{r}) - F_1(\mathbf{r})] * d(\mathbf{r}). \quad (4.2.3.20a)$$

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 (4.2.3.20a). In order to determine the diffuse scattering the Fourier transformation of (4.2.3.20a) is performed:

$$L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}). \quad (4.2.3.20b)$$

The intensity is given by

$$|L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2. \quad (4.2.3.20c)$$

Evaluation of equation (4.2.3.20c) yields three terms (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 $[l(\mathbf{r}) = l(-\mathbf{r}); b(\mathbf{r}) = b(-\mathbf{r}); \Delta F = F_2 - F_1]$:

$$\begin{aligned} & [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * d(\mathbf{r}) * [l(\mathbf{r})b(\mathbf{r})] * \Delta F^+(-\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})b(\mathbf{r})] * [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})t(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}). \quad (4.2.3.21a) \end{aligned}$$

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

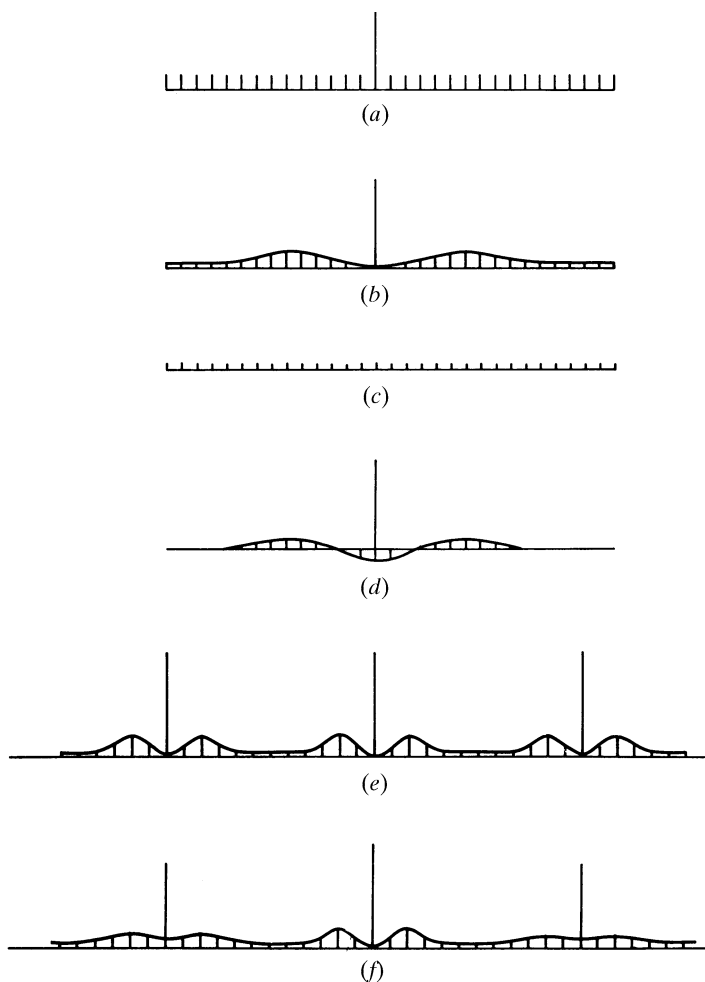


Fig. 4.2.3.2. One-dimensional Patterson functions of various point-defect distributions: (a) random distribution; (b) influence of finite volume of defects on the distribution function; (c), (d) decomposition of (b) into a periodic (c) and a convergent (d) part; (e) Fourier transform of (c) + (d); (f)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

dimension the solution of a random distribution of particles of a given size on a finite length shows that the distribution functions exhibit periodicities depending 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 (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 (= 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 which 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

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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).

(ii) There is no perfect lattice geometry. In this case a continuous Patterson function results. Fourier transformation yields an influence which 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 which 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 (size-independent random distribution).

The complete qualitative discussion of the diffraction pattern may be made by investigating the Fourier transform of (4.2.3.21a):

$$[L(\mathbf{H}) * T(\mathbf{H})] |\Delta F(\mathbf{H})|^2 |D(\mathbf{H})|^2. \quad (4.2.3.21b)$$

The first factor in (4.2.3.21b) 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 structure determination of domains, intensities near the Bragg peaks should be avoided. Note that equation (4.2.3.21b) may be used for measurements applying anomalous scattering in both the centric and the acentric case.

Solution of the diffraction problem. In equation (4.2.3.21b) $\Delta F(\mathbf{H})$ is replaced by its average

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

where p_{μ} represents the *a priori* probability of a domain of type μ . 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 in Al_2O_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 (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 (4.2.3.20c) which do 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

$$|\langle F(\mathbf{H}) \rangle|^2 = \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2 \quad (4.2.3.21c)$$

where p_{μ} is the *a priori* probability of the structure factor $F_{\mu}(\mathbf{H})$. It should be emphasized here that (4.2.3.21c) is independent of the distribution function $d(\mathbf{r})$, or its Fourier transform $D(\mathbf{H})$.

(2) Periodic 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 a different structure, is shown in Fig. 4.2.3.3. The size of the

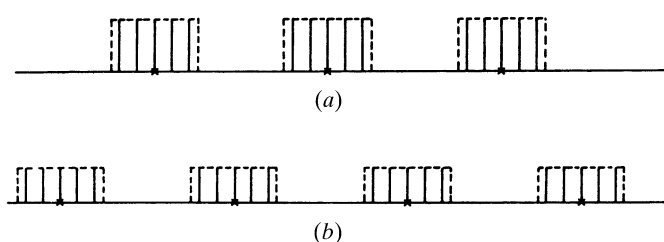


Fig. 4.2.3.3. Periodic array of domains consisting of two different atoms, represented by different heights. (a) Distribution of domain type 1, (b) distribution of domain type 2.

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:

$$\begin{aligned} & [l(\mathbf{r})b_1(\mathbf{r}) * d(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r}) * F_2(\mathbf{r}) \\ & = \{ [l(\mathbf{r})b_1(\mathbf{r}) + l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r}) \} * \langle F(\mathbf{r}) \rangle \\ & + [l(\mathbf{r})b_1(\mathbf{r}) - l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r}) * \Delta F(\mathbf{r})]. \end{aligned} \quad (4.2.3.22a)$$

Obviously the first term in curly brackets in equation (4.2.3.22a) 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 \mathbf{c} 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 (4.2.3.22a) yields

$$L(\mathbf{H}) \langle F(\mathbf{H}) \rangle + \{ L(\mathbf{H}) * [B_1(\mathbf{H}) - B_2(\mathbf{H})] \} D(\mathbf{H}) \Delta F(\mathbf{H}). \quad (4.2.3.22b)$$

The first term in equation (4.2.3.22b) 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. 4.2.3.3b). 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 for the position of the interface. This point is meaningless only in the case of a strictly periodic array of domains (no diffuse scattering). Therefore it seems to be convenient to introduce two basic 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 basic vectors and V' is the volume of the supercell. As long as the new basic 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 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.

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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 (4.2.3.21b,c) and (4.2.3.22b) we obtain, in the case of negligible short-range order, the following expressions for sharp and diffuse scattering (c = 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 both 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 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 and 2, respectively. 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. Hence, 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 1 and 2 atoms. 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 more or less sharp superstructure reflections. These are not observed on those rows of the reciprocal lattice which 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.

(3) *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 (4.2.3.22b) (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 = number of cells of 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 thickness of the domains. For this reason an accurate calculation of the amplitudes of satellites is necessary (Jagodzinski & Penzkofer, 1981):

(a) Bragg peaks of the basic lattice

$$I \sim |\langle F(\mathbf{H}) \rangle|^2; \quad (4.2.3.23a)$$

(b) satellites: $\nu = 2n$ (n = integer except 0)

$$I \sim |2 \sin \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2; \quad (4.2.3.23b)$$

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

$$I \sim |2 \cos \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2. \quad (4.2.3.23c)$$

ν = order of satellites, $C = \frac{1}{2}(N_1 - N_2)/(N_1 + N_2)$, N_1, N_2 = 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 (4.2.3.23b) 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 if $N_2 = 0$). The denominators in equations (4.2.3.23b,c) indicate a decrease in intensity with increasing order of satellites. The quantitative behaviour of the intensities needs a more detailed discussion of the numerator in equations (4.2.3.23a,b) with increasing order of 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 $\Delta F(\mathbf{H})$. Both have 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 well be represented by a multi-dimensional group-theoretical representation as has been shown by de Wolff (1974), Janner & Janssen (1980), de Wolff *et al.* (1981), and others.

(4) *Non-periodic system (qualitative discussion)*

Following the discussion of equations (4.2.3.21) one may conclude that the fluctuations of domain sizes cause a broadening of satellites, if the periodic distribution function has to be replaced by a statistical one. In this case the broadening effect increases with the order of 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 (4.2.3.23) shows that the position of the interface plays an important role for

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the intensities of 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 which 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 non-periodic 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 (4.2.3.23) for $N_1 = N_2$, consequently odd orders of satellites only 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

$$L_s(\mathbf{H})\{\Delta F_i(\mathbf{H}) \exp\{2\pi i N_1 H/2\} + \Delta F'_i(\mathbf{H}) \exp\{-2\pi i N_1 H/2\}\}, \quad (4.2.3.24)$$

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 ν th satellite, which may be calculated more accurately by taking into account the symmetry operations. The important difference between equations (4.2.3.23) and (4.2.3.24) is the missing decrease in intensity with increasing order of 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.

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

Obviously the preceding discussion of the diffuse scattering from domains is restricted to more or less small fluctuations of domain sizes. This is specifically valid if the most probable domain size

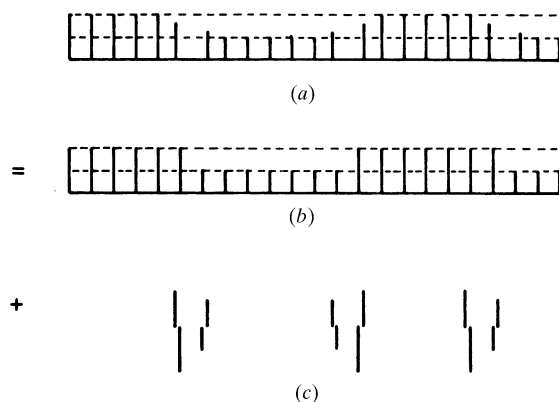


Fig. 4.2.3.4. Influence of distortions at the boundary of domains, and separation into two parts; for discussion see text.

does not differ markedly from the average size. The 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 $p_{\mu}p_{\mu'}(\mathbf{m})$ which may be derived from the pair-probability of nearest neighbours $p_{\mu}p_{\mu'}(\mathbf{1})$. (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

$$p_{11}(\mathbf{m}) = p_{22}(\mathbf{m}), \quad p_{12}(\mathbf{m}) = p_{21}(\mathbf{m}). \quad (4.2.3.25)$$

It may be derived from equation (4.2.3.25) that the *a priori* probabilities p_{μ} 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 $p_{11}(\mathbf{1})$ [$0 \leq p_{11}(\mathbf{1}) \leq 1$]:

$$p_{\mu} = \frac{1}{2} p_{11}(\mathbf{1})^{m-1} [1 - p_{11}(\mathbf{1})]. \quad (4.2.3.26)$$

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 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 (4.2.3.26) that the function $p_{11}(\mathbf{m})$ decreases monotonically with increasing \mathbf{m} , approaching $\frac{1}{2}$ with $\mathbf{m} \rightarrow \infty$. Apparently this cannot be true for a finite crystal if $p_{11}(\mathbf{m})$ is unity (structure of two types of domains) or zero (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 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). $p_{11}(\mathbf{m})$ 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 which has to be calculated. For a qualitative

4. DIFFUSE SCATTERING AND RELATED TOPICS

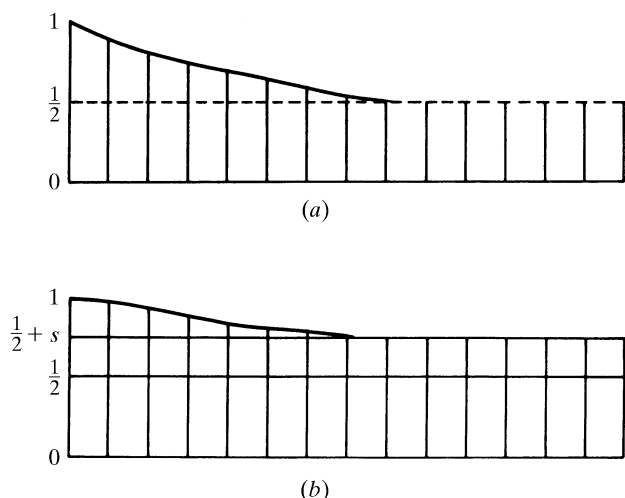


Fig. 4.2.3.5. Typical distributions of mixed crystals (unmixing): (a) upper curve: short-range order only; (b) lower curve: long-range order.

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 (4.2.3.25) are valid. The convolution in real space yields with factors $t(\mathbf{r})$ (equations 4.2.3.21):

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

where $p'_{\mu\mu'}(\mathbf{m})$ are factors attached to the δ 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 n in the δ functions results from the convolution with the inverted lattice [cf. Patterson (1959, equation 32)]. Fourier

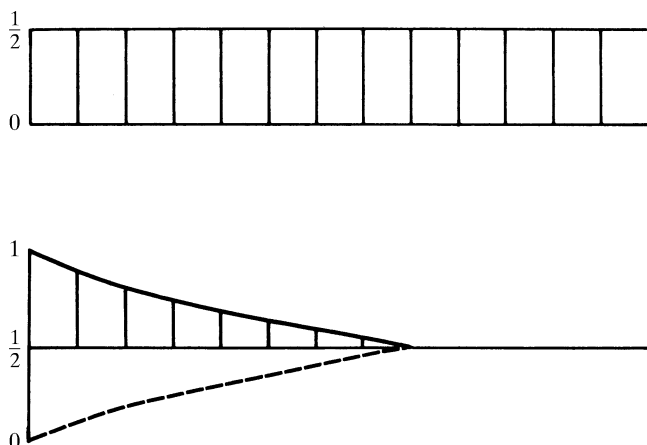


Fig. 4.2.3.6. Decomposition of Fig. 4.2.3.5(a) into a periodic and a rapidly convergent part.

transformation of the four terms given above yields the four corresponding expressions (μ, μ'):

$$\frac{1}{2}[T(\mathbf{H}) * \sum_{\mathbf{m}} p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i\mathbf{H} \cdot \mathbf{m}\}]F_{\mu}(\mathbf{H})F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27a)$$

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} :

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

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 (4.2.3.27a) results in

$$\frac{1}{2}[L(\mathbf{H}) * T(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H})]F_{\mu}(\mathbf{H})F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27b)$$

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 μ, μ'

$$I_d \approx [L(\mathbf{H}) * T(\mathbf{H}) * P'_{11}(\mathbf{H})]|\Delta F(\mathbf{H})|^2 \quad (4.2.3.28)$$

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 (4.2.3.21b) and (4.2.3.28). Equation (4.2.3.28) 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 (4.2.3.28) 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 increasing number of correlation functions. Here the cluster method seems to be more convenient and is discussed below.

(6) *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 $\frac{1}{2} + s$, the *a priori* probability changes correspondingly. Since $p_{12}(\infty)$ becomes $\frac{1}{2} - s$, the symmetry relation given in equation (4.2.3.25) 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, $p_{22}(\infty) = \frac{1}{2} + s$, $p_{21}(\infty) = \frac{1}{2} - s$, respectively, 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.

$$\begin{aligned} I_1 &\sim |(\frac{1}{2} + s)F_1(\mathbf{H}) + (\frac{1}{2} - s)F_2(\mathbf{H})|^2 \\ I_2 &\sim |(\frac{1}{2} + s)F_2(\mathbf{H}) + (\frac{1}{2} - s)F_1(\mathbf{H})|^2, \end{aligned} \quad (4.2.3.29)$$

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

$$I = (I_1 + I_2)/2. \quad (4.2.3.30)$$

Introducing equation (4.2.3.29) into (4.2.3.30) we obtain

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

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

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

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

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

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

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

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

With the definitions introduced above it is found that:

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

The diffuse scattering is given by:

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

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

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

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

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

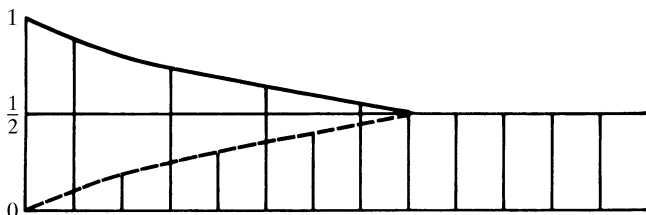


Fig. 4.2.3.7. The same distribution (cf. Fig. 4.2.3.5) in the case of superstructure formation.

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

Sharp Bragg reflections

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

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

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

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

Diffuse reflections

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

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

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

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

(8) *Order-disorder in three dimensions*

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

N subcells in real space are assumed, each of them representing a kind of a complicated 'atom' which may be equal by translation or other symmetry operation. Once a superspace group has been determined, the usual extinction rules of space groups may be applied, remembering that the 'atoms' themselves may have systematic extinctions. Major difficulties arise from the existence of different symmetries of the subgroup and the supergroup. Since the symmetry of the supergroup is lower in general, all missing

symmetry elements may cause domains, corresponding to the missing symmetry element: translations cause antiphase domains in their generalized sense, other symmetry elements cause twins generated by rotations, mirror planes or the centre of symmetry. If all these domains are small enough to be detected by a careful study of line profiles, using diffraction methods with a high resolution power, the structural study may be facilitated by a reasonable explanation of scaling factors to be introduced for groups of reflections affected by the possible domain structures.

(9) Density modulations

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

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

Fourier transformation yields

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

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 $n\Delta\mathbf{H}$ ($n = \text{integer}$) does not coincide with a main reflection in reciprocal space, the modulated structure is incommensurate with the basic lattice, and the phase of the density wave becomes meaningless. The same is true for the relative phases of the various orders of harmonic modulations of the density. This uncertainty even remains valid for commensurate density modulations of the sublattice, because coinciding higher-order harmonics in reciprocal space cause the same difficulty; higher-order coefficients cannot uniquely be separated from lower ones, consequently structure determination becomes impossible unless phase-determination methods are applied. Fortunately, density modulations of pure harmonic character are impossible for chemical reasons; they may be approximated by disorder phenomena for the averaged structure only. If diffuse scattering is taken into account the situation is changed considerably: A careful study of the diffuse scattering alone, although difficult in principle, will yield the necessary information about the relative phases of density waves (Korekawa, 1967).

(10) Displacement modulations

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

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

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

4.2.3.2. Guideline to solve a disorder problem

Generally, structure determination of a disordered crystal should start in the usual way by solving the average structure. The effectiveness of this procedure strongly depends on the distribution of integrated intensities of sharp and diffuse reflections. In cases where the integrated intensities of Bragg peaks is predominant, the maximum information can be drawn from the averaged structure. The observations of fractional occupations of lattice sites, split positions and anomalous temperature factors are indications of the disorder involved. Since these aspects of disorder phenomena in the averaged structure may be interpreted very easily, a detailed discussion of this matter is not given here (see any modern textbook of X-ray crystallography).

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

(a) The diffuse scattering is concentrated near the Bragg peaks for a large number of reflections. Because of the limited resolution power of conventional single-crystal methods the separation of sharp and diffuse scattering is impossible. Hence, the conventional study of integrated intensities does not really lead to an averaged structure. In this case a refinement should be tried using an incoherent superposition of different structure factors. Application