

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 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 (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 ΔF 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

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

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

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

where (Δf) 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 α_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