

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

intensity. The second term causes an antisymmetrical contribution to intensity profiles but does not influence the integrated intensities. These general relations enable a semi-quantitative interpretation of the sharp and diffuse scattering in any case, without performing the time-consuming calculations of the constants which may only be done in more complicated disorder problems with the aid of a computer program evaluating the boundary conditions of the problem.

This can be carried out with the aid of the characteristic values and a linear system of equations (Jagodzinski, 1949*a,b,c*), or with the aid of matrix formalism (Kakinoki & Komura, 1954; Takaki & Sakurai, 1976). As long as only the line profiles and positions of the reflections are required, these quantities may be determined experimentally and fitted to characteristic values of a matrix. The size of this matrix is given by the number of sharp and diffuse maxima observed, while $|\lambda_\nu|$ and $\exp\{2\pi i\varphi_\nu\}$ may be found by evaluating the line width and the position of diffuse reflections. Once this matrix has been found, a semi-quantitative model of the disorder problem can be given. If a system of sharp reflections is available, the averaged structure can be solved as described in Section 4.2.3.2. The determination of the constants of the diffraction problem is greatly facilitated by considering the intensity modulation of diffuse scattering, which enables a phase determination of structure factors to be made under certain conditions.

The theory of closed-packed structures with three equivalent translation vectors has been applied very frequently, even to systems which do not obey the principle of close-packing. The first quantitative explanation was published by Halla *et al.* (1953). It was shown there that single crystals of $C_{18}H_{24}$ from the same synthesis may have a completely different degree of order. This was true even within the same crystal. Similar results were found for C, Si, CdI_2 , CdS_2 , mica and many other compounds. Quantitative treatments are less abundant [*e.g.* CdI_2 : Martorana *et al.* (1986); MX_3 structures: Conradi & Müller (1986)]. Special attention has been paid to the quantitative study of polytypic phase transformations in order to gain information about the thermodynamical stability or the mechanism of layer displacements, *e.g.* Co (Edwards & Lipson, 1942; Frey & Boysen, 1981), SiC (Jagodzinski, 1972; Pandey *et al.*, 1980), ZnS (Müller, 1952; Mardix & Steinberger, 1970; Frey *et al.*, 1986) and others.

Certain laws may be derived for the reduced integrated intensities of diffuse reflections. ‘Reduction’ in this context means a division of the diffuse scattering along l by the structure factor, or the difference structure factor if $\langle F \rangle \neq 0$. This procedure is valuable if the number of stacking faults rather than the complete solution of the diffraction problem is required.

The discussion given above has been made under the assumption that the full symmetry of the layers is maintained in the statistics. Obviously, this is not necessarily true if external lower symmetries influence the disorder. An important example is the generation of stacking faults during plastic deformation. Problems of this kind need a complete reconsideration of symmetries. Furthermore, it should be pointed out that a treatment with the aid of an extended Ising model as described above is irrelevant in most cases. Simplified procedures describing the diffuse scattering of intrinsic, extrinsic, twin stacking faults and others have been described in the literature. Since their influence on *structure determination* can generally be neglected, the reader is referred to the literature for additional information.

4.2.4.3. Two-dimensional disorder of chains

In this section disorder phenomena are considered which are related to chain-like structural elements in crystals. This topic includes the so-called ‘1D crystals’ where translational symmetry

(in direct space) exists in one direction only – crystals in which highly anisotropic binding forces are responsible for chain-like atomic groups, *e.g.* compounds which exhibit a well ordered 3D framework structure with tunnels in a unique direction in which atoms, ions or molecules are embedded. Examples are compounds with platinum, iodine or mercury chains, urea inclusion compounds with columnar structures (organic or inorganic), 1D ionic conductors, polymers *etc.* Diffuse-scattering studies of 1D conductors have been carried out in connection with investigations of stability/instability problems, incommensurate structures, phase transitions, dynamic precursor effects *etc.* These questions are not treated here. For general reading of diffuse scattering in connection with these topics see, *e.g.*, Comes & Shirane (1979, and references therein). Also excluded are specific problems related to polymers or liquid crystals (mesophases) (see Chapter 4.4) and magnetic structures with chain-like spin arrangements.

Trivial diffuse scattering occurs as 1D Bragg scattering (diffuse layers) by internally ordered chains. Diffuse phenomena in reciprocal space are due to ‘longitudinal’ disordering within the chains (along the unique direction) as well as to ‘transverse’ correlations between different chains over a restricted volume. Only static aspects are considered; diffuse scattering resulting from collective excitations or diffusion-like phenomena which are of inelastic or quasielastic origin are not treated here.

4.2.4.3.1. Scattering by randomly distributed collinear chains

As found in any elementary textbook of diffraction the simplest result of scattering by a chain with period c

$$I(\mathbf{r}) = I(z) = \sum_{n_3} \delta(z - n_3c) \quad (4.2.4.12)$$

is described by one of the Laue equations:

$$G(L) = |L(L)|^2 = \sin^2 \pi N L / \sin^2 \pi L \quad (4.2.4.13)$$

which gives broadened profiles for small N . In the context of phase transitions the Ornstein–Zernike correlation function is frequently used, *i.e.* (4.2.4.13) is replaced by a Lorentzian:

$$1/\{\xi^2 + 4\pi^2(L-l)^2\}, \quad (4.2.4.14)$$

where ξ denotes the correlation length.

In the limiting case $N \rightarrow \infty$, (4.2.4.13) becomes

$$\sum_l \delta(L-l). \quad (4.2.4.15)$$

The scattering by a real chain $a(\mathbf{r})$ consisting of molecules with structure factor F_M is therefore determined by

$$F_M(\mathbf{H}) = \sum_j f_j \exp\{2\pi i(Hx_j + Ky_j + Lz_j)\}. \quad (4.2.4.16)$$

The Patterson function is:

$$P(\mathbf{r}) = (1/c) \int \int |F_0(H, K)|^2 \cos 2\pi(Hx + Ky) dH dK \\ + (2/c) \sum_l \int \int |F_l|^2 \exp\{2\pi i(Hx + Ky)\} \\ \times \exp\{-2\pi ilz\} dH dK, \quad (4.2.4.17)$$

where the index l denotes the only relevant position $L = l$ (the subscript M is omitted).

The intensity is concentrated in diffuse layers perpendicular to \mathbf{c}^* from which the structural information may be extracted. Projections are:

$$\int a(\mathbf{r}) dz = \int \int F_0(H, K) \exp\{2\pi i(Hx + Ky)\} dH dK \quad (4.2.4.18)$$

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$$\int \int a(\mathbf{r}) \, dx \, dy = (2/c) \sum_l F_l(00l) \exp(-2\pi i l z). \quad (4.2.4.19)$$

Obviously the z parameters can be determined by scanning along a meridian (00L) through the diffuse sheets (diffractometer recording). Owing to intersection of the Ewald sphere with the set of planes the meridian cannot be recorded on *one* photograph; successive equi-inclination photographs are necessary. Only in the case of large c spacings is the meridian well approximated in one photograph.

There are many examples where a tendency to cylindrical symmetry exists: chains with p -fold rotational or screw symmetry around the preferred direction or assemblies of chains (or domains) with statistical orientational distribution around the texture axis. In this context it should be mentioned that symmetry operations with rotational parts belonging to the 1D rod groups actually occur, *i.e.* not only $p = 2, 3, 4, 6$.

In all these cases a treatment in the frame of cylindrical coordinates is advantageous (see, *e.g.*, Vainshtein, 1966):

Direct space	Reciprocal space
$x = r \cos \psi$	$H = H_r \cos \Psi$
$y = r \sin \psi$	$K = H_r \sin \Psi$
$z = z$	$L = L$

$$a(r, \psi, z) = \int \int \int F(\mathbf{H}) \exp\{-2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \times H_r \, dH_r \, d\Psi \, dL \quad (4.2.4.20)$$

$$F(\mathbf{H}) = \int \int \int a(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \times r \, dr \, d\psi \, dz. \quad (4.2.4.21)$$

The integrals may be evaluated by the use of Bessel functions:

$$J_n(u) = \frac{1}{2\pi i^n} \int \exp\{i(u \cos \varphi + n\varphi)\} \, d\varphi$$

($u = 2\pi r H_r$; $\varphi = \psi - \Psi$).

The 2D problem $a = a(r, \psi)$ is treated first; an extension to the general case $a(r, \psi, z)$ is easily made afterwards.

Along the theory of Fourier series one has:

$$\begin{aligned} a(r, \psi) &= \sum_n a_n(r) \exp\{in\psi\} \\ a_n(r) &= \frac{1}{2\pi} \int a(r, \psi) \exp\{-in\psi\} \, d\psi \end{aligned} \quad (4.2.4.22)$$

or with:

$$\begin{aligned} \alpha_n &= \frac{1}{2\pi} \int a(r, \psi) \cos(n\psi) \, d\psi \\ \beta_n &= \frac{1}{2\pi} \int a(r, \psi) \sin(n\psi) \, d\psi \\ a_n(r) &= |a_n(r)| \exp\{-i\psi_n(r)\} \\ |a_n(r)| &= \sqrt{\alpha_n^2 + \beta_n^2} \\ \psi_n(r) &= \arctan \beta_n / \alpha_n. \end{aligned}$$

If contributions to anomalous scattering are neglected $a(r, \psi)$ is a real function:

$$a(r, \psi) = \sum_n |a_n(r)| \cos[n\psi - \psi_n(r)]. \quad (4.2.4.23)$$

Analogously, one has

$$F(H_r, \Psi) = \sum_n |F_n(H_r)| \exp(in\Psi). \quad (4.2.4.24)$$

$F(H_r, \Psi)$ is a complex function; $F_n(H_r)$ are the Fourier coefficients which are to be evaluated from the $a_n(r)$:

$$\begin{aligned} F_n(H_r) &= \frac{1}{2\pi} \int F(H_r, \Psi) \exp\{-in\Psi\} \, d\Psi \\ &= \exp\{in\pi/2\} \int a_n(r) J_n(2\pi r H_r) 2\pi r \, dr \\ F(H_r, \Psi) &= \sum_n \exp\{in[\Psi + (\pi/2)]\} \int a_n(r) \\ &\quad \times J_n(2\pi r H_r) 2\pi r \, dr \end{aligned} \quad (4.2.4.25)$$

$$\begin{aligned} a(r, \psi) &= \sum_n \exp\{in[\Psi - (\pi/2)]\} \int F_n(H_r) \\ &\quad \times J_n(2\pi r H_r) 2\pi H_r \, dH_r. \end{aligned} \quad (4.2.4.26)$$

The formulae may be used for calculation of diffuse intensity distribution within a diffuse sheet, in particular when the chain molecule is projected along the unique axis [*cf.* equation (4.2.4.18)].

Special cases are:

(a) *Complete cylinder symmetry*

$$F(H_r) = 2\pi \int a(r) J_0(2\pi r H_r) r \, dr \quad (4.2.4.27)$$

$$a(r) = 2\pi \int F(H_r) J_n(2\pi r H_r) H_r \, dH_r. \quad (4.2.4.28)$$

(b) *p-fold symmetry of the projected molecule* $a(r, \psi) = a[r, \psi + (2\pi/p)]$

$$\begin{aligned} F_p(H_r, \Psi) &= \sum_n \exp\{inp[\Psi + (\pi/2)]\} \\ &\quad \times \int a_{np}(r) J_{np}(2\pi r H_r) 2\pi r \, dr \end{aligned} \quad (4.2.4.29)$$

$$a_p(r, \psi) = \sum_n |a_{np}(r)| \cos[np\psi - \psi_{np}(r)]. \quad (4.2.4.30)$$

Only Bessel functions J_0, J_p, J_{2p}, \dots occur. In most cases J_{2p} and higher orders may be neglected.

(c) *Vertical mirror planes*

Only cosine terms occur, *i.e.* all $\beta_n = 0$ or $\psi_n(r) = 0$.

The *general 3D expressions* valid for extended chains with period c [equation (4.2.4.12)] are found in an analogous way:

$$a(r, \psi, z) = a_M(r, \psi, z) * l(z)$$

$$\begin{aligned} F(\mathbf{H}) &= F_l(H_r, \Psi, L) = F_M(\mathbf{H})L(L) \\ &= \int \int \int a_M(r, \psi, z) \exp\{2\pi i [H_r r \cos(\psi - \Psi) + Lz]\} \\ &\quad \times 2\pi r \, dr \, d\psi \, dz \end{aligned} \quad (4.2.4.31)$$

using a series expansion analogous to (4.2.4.23) and (4.2.4.24):

$$a_{nl}(r) = \frac{1}{2\pi} \int \int a_M \exp\{-i(n\psi - 2\pi lz)\} \, d\psi \, dz \quad (4.2.4.32)$$

$$F_{nl}(H_r) = \exp\{in\pi/2\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr \quad (4.2.4.33)$$

one has:

$$F_l(\mathbf{H}) = \sum_n \exp\{in[\Psi + (\pi/2)]\} \int a_{nl}(r) J_n(2\pi H_r r) 2\pi r \, dr. \quad (4.2.4.34)$$

In practice the integrals are often replaced by discrete summation of j atoms at positions: $r = r_j, \psi = \psi_j, z = z_j$ ($0 \leq z_j < c$):

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$$F_l(\mathbf{H}) = \sum_j \sum_n f_j J_n(2\pi H_r r_j) \exp\{-in\psi_j\} \\ \times \exp(2\pi i l z_j) \exp\{in[\Psi + (\pi/2)]\} \quad (4.2.4.35)$$

or

$$F_l(\mathbf{H}) = \sum_n (\alpha_n + i\beta_n) \exp\{in\Psi\} \\ \alpha_n = \sum_j f_j J_n(2\pi H_r r_j) \cos\{n[(\pi/2) - \psi_j] + 2\pi l z_j\} \\ \beta_n = \sum_j f_j J_n(2\pi H_r r_j) \sin\{n[(\pi/2) - \psi_j] + 2\pi l z_j\}.$$

Intensity in the l th diffuse layer is given by

$$I_l = \sum_n \sum_{n'} [(\alpha_n \alpha_{n'} + \beta_n \beta_{n'}) + i(\alpha_{n'} \beta_n - \alpha_n \beta_{n'})] \\ \times \exp\{i(n - n')\Psi\}. \quad (4.2.4.36)$$

(a) *Cylinder symmetry* (free rotating molecules around the chain axis or statistical averaging with respect to ψ over an assembly of chains). Only component F_{0l} occurs:

$$F_{0l}(H_r, L) = 2\pi \int \int \langle a_M \rangle J_0(2\pi H_r r) \exp\{2\pi i l z\} r \, dr \, dz$$

or

$$F_{0l}(H_r, L) = \sum_j f_j J_0(2\pi H_r r_j) \exp\{2\pi i l z_j\}.$$

In particular, $F_{00}(H_r)$ determines the radial component of the molecule projected along z :

$$F_{00}(H_r) = \sum_j f_j J_0(2\pi H_r r_j).$$

(b) *p-fold symmetry* of a plane molecule (or projected molecule) as outlined previously: only components np instead of n occur. Bessel functions J_0 and J_p are sufficient in most cases.

(c) *Vertical mirror plane*: see above.

(d) *Horizontal mirror plane* (perpendicular to the chain): Exponentials $\exp\{2\pi i l z\}$ in equation (4.2.4.32) may be replaced by $\cos 2\pi l z$.

(e) *Twofold symmetry axis* perpendicular to the chain axis (at positions $\psi = 0, 2\pi/p, \dots$). Exponentials in equation (4.2.4.32), $\exp\{-i(np\psi - 2\pi l z)\}$, are replaced by the corresponding cosine term $\cos(np\psi + 2\pi l z)$.

Formulae concerning the reverse method (Fourier synthesis) are not given here (see, e.g., Vainshtein, 1966). Usually there is no practical use in diffuse-scattering work because it is very difficult to separate out a single component F_{nl} . Every diffuse layer is affected by *all* components F_{nl} . There is a chance if *one* diffuse layer corresponds predominantly to *one* Bessel function.

4.2.4.3.2. Disorder within randomly distributed collinear chains

Deviations from strict periodicities in the z direction within one chain may be due to loss of translational symmetry of the centres of the molecules along z and/or due to varying orientations of the molecules with respect to different axes, such as azimuthal misorientation, tilting with respect to the z axis or combinations of both types. As in 3D crystals, there may or may not exist 1D structures in an averaged sense.

4.2.4.3.2.1. General treatment

All formulae given in this section are only special cases of a 3D treatment (see, e.g., Guinier, 1963). The 1D lattice (4.2.4.12) is

replaced by a distribution:

$$d(z) = \sum_\nu \delta(z - z_\nu) \\ D(L) = \sum_\nu \exp\{2\pi i L z_\nu\} \quad (4.2.4.37)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})D(L).$$

The Patterson function is given by

$$P(\mathbf{r}) = [a_M(\mathbf{r}) * a_M - (\mathbf{r})] * [d(z) * d - (z)]. \quad (4.2.4.38)$$

Because the autocorrelation function $w = d * d$ is centrosymmetric

$$w(z) = N\delta(z) + \sum_\nu \sum_\mu \delta[z - (z_\nu - z_\mu)] + \sum_\nu \sum_\mu \delta[z + (z_\nu - z_\mu)], \quad (4.2.4.39)$$

the interference function $W(L) (= |D(L)|^2)$ is given by

$$W(L) = N + 2 \sum_\nu \sum_\mu \cos 2\pi [L(z_\nu - z_\mu)] \quad (4.2.4.40)$$

$$I(\mathbf{H}) = |F_M(\mathbf{H})|^2 W(L). \quad (4.2.4.41)$$

Sometimes, e.g. in the following example of orientational disorder, there is an order only within domains. As shown in Section 4.2.3, this may be treated by a box or shape function $b(z) = 1$ for $z \leq z_N$ and 0 elsewhere.

$$d(z) = d_\infty b(z) \\ a(\mathbf{r}) = a_M(\mathbf{r}) * [d_\infty b(z)] \quad (4.2.4.42)$$

$$F(\mathbf{H}) = F_M(\mathbf{H})[D_\infty * B(L)]$$

with

$$b(z) * b - (z) \leftrightarrow |B(L)|^2 \\ I = |F_M(\mathbf{H})|^2 |D_\infty * B(L)|^2. \quad (4.2.4.43)$$

If the order is perfect within one domain one has $D_\infty(L) \simeq \sum \delta(L - l)$; $(D_\infty * B) = \sum D(L - l)$; i.e. each reflection is affected by the shape function.

4.2.4.3.2.2. Orientational disorder

A misorientation of the chain molecules with respect to one another is taken into account by different structure factors F_M .

$$I(\mathbf{H}) = \sum_\nu \sum_\mu F_\nu(\mathbf{H}) F_\mu(\mathbf{H})^+ \exp\{2\pi i L(z_\nu - z_\mu)\}. \quad (4.2.4.44)$$

A further discussion follows the same arguments outlined in Section 4.2.3. For example, a very simple result is found in the case of uncorrelated orientations. Averaging over all pairs $F_\nu F_\mu^+$ yields

$$I(\mathbf{H}) = N(\langle |F|^2 \rangle - \langle |F|^2 \rangle) + \langle |F|^2 \rangle L(L), \quad (4.2.4.44a)$$

where

$$\langle |F|^2 \rangle = 1/N^2 \langle F_\nu F_\mu^+ \rangle \\ = \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_\mu \alpha_\mu F_\mu^+(\mathbf{H}) \quad (\nu \neq \mu) \\ \langle |F|^2 \rangle = 1/N \langle F_\nu F_\nu^+ \rangle = \sum_\nu \alpha_\nu |F_\nu(\mathbf{H})|^2.$$

Besides the diffuse layer system there is a diffuse background modulated by the \mathbf{H} dependence of $[\langle |F(\mathbf{H})|^2 \rangle - \langle |F(\mathbf{H})|^2 \rangle]$.