4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

behaviour, there is also a displacement component parallel to the plane of intergrowth in question. The semi-quantitative interpretation has been given in his paper.

(3) *Rotations*

The discussion concerning layers related by a twofold rotation parallel to **c** may easily be made by simply considering their structure factors. Since the layers do not obey the twofold symmetry their structure factors are generally different; unless they equalize accidentally there are sharp and diffuse reflections according to the values of $\langle F \rangle$ and ΔF, respectively. Obviously, $F_1 = F_2$ is valid only if $h = k = 0$; consequently there is just one reciprocal-lattice row free from diffuse scattering.

(4) *Asymmetric case*

In the asymmetric case the symmetry conditions used above are no longer valid:

$$p_1 \neq p_2, p_{12} \neq p_{21}, p_{11} \neq p_{22}.$$

But there is one condition which may be derived from the invariance of the numbers of pairs in the relevant and its opposite direction:

$$p_\mu p_{\mu\mu'}(\mathbf{m}) = p_{\mu'} p_{\mu'\mu}(-\mathbf{m}).$$

This equation requires that $p_{\mu\mu'}(\mathbf{m})$ is not necessarily symmetric in **m**. The calculation of characteristic values yields

$$\lambda_1 = 1, \qquad \lambda_2 = (\alpha_1 + \alpha_2) - 1. \qquad (4.2.4.6)$$

The *a priori* probabilities are now different from $\frac{1}{2}$, and may be calculated by considering $p_{\mu\mu'}(\mathbf{m}) \rightarrow p_{\mu'}(\mathbf{m} \rightarrow \infty)$:

$$p_1 = \alpha_1/(\alpha_1 + \alpha_2); \qquad p_2 = \alpha_2/(\alpha_1 + \alpha_2).$$

The intensity is given by an expression very similar to (4.2.4.5):

$$I(\mathbf{H}) = L(\mathbf{h})|[\alpha_1/(\alpha_1 + \alpha_2)]F_1 + [\alpha_2/(\alpha_1 + \alpha_2)]F_2|^2$$
$$+ L(h,k)|[\alpha_1/(\alpha_1 + \alpha_2)]F_1 - [\alpha_2/(\alpha_1 + \alpha_2)]F_2|^2$$
$$\times (1 - |\lambda_2|^2)/(1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2). \qquad (4.2.4.7)$$

Again there are sharp Bragg reflections and diffuse ones in the same positions, or in a displaced position depending on the sign of λ_2.

From a discussion of the next-nearest-neighbour Ising model one may conclude that the detailed study of the qualitative behaviour of sharp and diffuse reflections may give additional information on the symmetry of the layers involved.

In the case of translations between neighbouring layers not fulfilling the condition $\mathbf{h} \cdot \mathbf{r} = $ integer, where **r** is parallel to the layer, more than two structure factors have to be taken into account. If $n\mathbf{h} \cdot \mathbf{r} = $ integer, where n is the smallest integer fulfilling the said condition, n different structure factors have to be considered. The characteristic equation has formally to be derived with the aid of an $n \times n$ matrix containing internal symmetries which may be avoided by adding the phase factors $\varepsilon = \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}/n\}$, $\varepsilon^+ = \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r}/n\}$ to the probability of pairs. The procedure is allowed if the displacements **r** and $-\mathbf{r}$ are admitted only for neighbouring layers. The matrix yielding the characteristic values may then be reduced to

$$\begin{pmatrix} \alpha_1 \varepsilon & (1 - \alpha_1)\varepsilon^+ \\ (1 - \alpha_2)\varepsilon & \alpha_2 \varepsilon^+ \end{pmatrix}$$

and yields the characteristic equation

$$\lambda^2 - \lambda(\alpha_1 \varepsilon + \alpha_2 \varepsilon^+) - 1 + \alpha_1 + \alpha_2 = 0. \qquad (4.2.4.8)$$

Equation (4.2.4.8) gives sharp Bragg reflections for $\mathbf{H} \cdot \mathbf{r}/n = $ integer; the remaining diffuse reflections are displaced

corresponding to the phase of the complex characteristic value. Equation (4.2.4.8) has been used in many cases. Qualitative examples are the mixed-layer structures published by Hendricks & Teller (1942). An example of a four-layer-type structure is treated by Dubernat & Pezerat (1974). A first quantitative treatment with good agreement between theory and experimental data (powder diffraction) has been given by Dorner & Jagodzinski (1972) for the binary system TiO$_2$–SnO$_2$. In the range of the so-called spinodal decomposition the chemical composition of the two domains and the average lengths of the two types of domains could be determined. Another quantitative application was reported by Jagodzinski & Hellner (1956) for the transformation of RhSn$_2$ into a very complicated mixed-layer type. A good agreement of measured and calculated diffuse scattering (asymmetric line profiles, displacement of maxima) could be found over a wide angular range of single-crystal diffraction.

4.2.4.2.1. *Stacking disorder in close-packed structures*

From an historical point of view stacking disorder in close-packed systems is most important. The three relevant positions of ordered layers are represented by the atomic coordinates $|0,0|, |\frac{1}{3}, \frac{2}{3}|, |\frac{2}{3}, \frac{1}{3}|$ in the hexagonal setting of the unit cell, or simply by the figures 1, 2, 3 in the same sequence. Structure factors F_1, F_2, F_3 refer to the corresponding positions of the same layer:

$$F_2 = F_1 \exp\{2\pi i(h - k)/3\},$$
$$F_3 = F_1 \exp\{-2\pi i(h - k)/3\},$$

hence

$$F_1 = F_2 = F_3 \quad \text{if } h - k \equiv 0 \ (\text{mod } 3).$$

According to the above discussion the said indices define the reciprocal-lattice rows exhibiting sharp reflections only, as long as the distances between the layers are exactly equal. The symmetry conditions caused by the translation are normally:

$$p_1 = p_2 = p_3, \qquad p_{11} = p_{22} = p_{33},$$
$$p_{12} = p_{23} = p_{31}, \qquad p_{13} = p_{21} = p_{32}.$$

For the case of close packing of spheres and some other problems any configuration of **m** layers determining the *a posteriori* probability $p_{\mu\mu'}(\mathbf{m}), \mu = \mu'$, has a symmetrical counterpart where μ is replaced by $\mu' + 1$ (if $\mu' = 3, \mu' + 1 = 1$).

In this particular case $p_{12}(\mathbf{m}) = p_{13}(\mathbf{m})$, and equivalent relations generated by translation.

Nearest-neighbour interactions do not lead to an ordered structure if the principle of close packing is obeyed (no pairs in equal positions) (Hendricks & Teller, 1942; Wilson, 1942). Extension of the interactions to next-but-one or more neighbours may be carried out by introducing the method of matrix multiplication developed by Kakinoki & Komura (1954, 1965), or the method of overlapping clusters (Jagodzinski, 1954). The latter procedure is outlined in the case of interactions between four layers. A given set of three layers may occur in the following 12 combinations:

$$123, 231, 312; \quad 132, 213, 321;$$
$$121, 232, 313; \quad 131, 212, 323.$$

Since three of them are equivalent by translation, only four representatives have to be introduced:

$$123; \quad 132; \quad 121; \quad 131.$$

In the following the new indices 1, 2, 3, 4 are used for these four representatives for the sake of simplicity.

In order to construct the statistics layer by layer the next layer must belong to a triplet starting with the same two symbols with which the preceding one ended, *e.g.* 123 can only be followed by 231, or 232. In a similar way 132 can only be followed by 321 or 323. Since both cases are symmetrically equivalent the probabilities α_1 and $1 - \alpha_1$ are introduced. In a similar way 121 may be followed by 212 or 213 *etc.* For these two groups the probabilities α_2 and $1 - \alpha_2$ are defined. The different translations of groups are considered by introducing the phase factors as described above. Hence, the matrix for the characteristic equation may be set up as follows. As representative cluster of each group is chosen that one having the number 1 at the centre, *e.g.* 312 is representative for the group 123, 231, 312; in a similar way 213, 212 and 313 are the remaining representatives. Since this arrangement of three layers is equivalent by translation, it may be assumed that the structure of the central layer is not influenced by the statistics to a first approximation. The same arguments hold for the remaining three groups. On the other hand, the groups 312 and 213 are equivalent by rotation only. Consequently their structure factors may differ if the influence of the two neighbours has to be taken into account. A different situation exists for the groups 212 and 313 which are correlated by a centre of symmetry, which causes different corresponding structure factors. It should be pointed out, however, that the structure factor is invariant as long as there is no influence of neighbouring layers on the structure of the central layer. The latter is often observed in close-packed metal structures, or in compounds like ZnS, SiC and others. For the calculation of intensities $p_\mu p_{\mu\mu'}, F_\mu F_{\mu'}^+$ is needed.

According to the following scheme of sequences any sequence of pairs is correlated with the same phase factor for FF^+ due to translation, if both members of the pair belong to the same group. Consequently the phase factor may be attached to the sequence probability such that FF^+ remains unchanged, and the group may be treated as a single element in the statistics. In this way the reduced matrix for the solution of the characteristic equation is given by

reflections for $l =$ integer, and diffuse ones in a position determined by the sequence probabilities α_1 and α_2 (position either $l =$ integer, $l = \frac{1}{2} +$ integer, respectively). The remaining two characteristic values may be given in the form $\lambda = |\lambda| \exp\{2\pi i\varphi\}$, where φ determines the position of the reflection. If the structure factors of the layers are independent of the cluster, $\lambda_2, \lambda_3, \lambda_4$ become irrelevant because of the new identity of the F's (no diffuse scattering). Weak diffuse intensities on the lattice rows $k - k = 0$ (mod 3) may be explained in terms of this influence.

(2) The remaining two solutions for $\varepsilon = \exp\{\pm 2\pi i(h - k)/3\}$ are equivalent, and result in the same characteristic values. They have been discussed explicitly in the literature; the reader is referred to the papers of Jagodzinski (1949*a,b,c*, 1954).

In order to calculate the intensities one has to reconsider the symmetry of the clusters, which is different from the symmetry of the layers. Fortunately, a threefold rotation axis is invariant against the translations, but this is not true for the remaining symmetry operations in the layer if there are any more. Since we have two pairs of inequivalent clusters, namely 312, 213 and 212, 313, there are only two different *a priori* probabilities $p_1 = p_3$ and $p_2 = p_4 = \frac{1}{2}(1 - 2p_1)$.

The symmetry conditions of the new clusters may be determined by means of the so-called 'probability trees' described by Wilson (1942) and Jagodzinski (1949*b*, pp. 208–214). For example: $p_{11} = p_{33}, p_{22} = p_{44}, p_{13} = p_{31}, p_{24} = p_{42}$ *etc.*

It should be pointed out that clusters 1 and 3 describe a cubic arrangement of three layers in the case of simple close packing, while clusters 2 and 4 represent the hexagonal close packing. There may be a small change in the lattice constant c perpendicular to the layers. Additional phase factors then have to be introduced in the matrix for the characteristic equation, and a recalculation of the constants is necessary. As a consequence, the reciprocal-lattice rows $(h - k) \equiv 0$ (mod 3) become diffuse if $l \neq 0$, and the diffuseness increases with l. A similar behaviour results for the remaining reciprocal-lattice rows.

F_μ \ $F_{\mu'}^+$	(1) 312, 123(ε^+), 231(ε)	(2) 212, 323(ε^+), 131(ε)	(3) 213, 321(ε^+), 132(ε)	(4) 313, 121(ε^+), 232(ε)
(1) 312, 123(ε), 231(ε^+)	$\alpha_1\varepsilon^+$	0	0	$(1-\alpha_1)\varepsilon^+$
(2) 212, 323(ε), 131(ε^+)	$(1-\alpha_2)\varepsilon^+$	0	0	$\alpha_2\varepsilon^+$
(3) 213, 321(ε), 132(ε^+)	0	$(1-\alpha_2)\varepsilon$	$\alpha_1\varepsilon$	0
(4) 313, 121(ε), 232(ε^+)	0	$\alpha_2\varepsilon$	$(1-\alpha_2)\varepsilon$	0

There are three solutions of the diffraction problem:
(1) If $h - k = 0$ (mod 3), $\varepsilon = +1$, there are two quadratic equations:

$$\lambda^2 - (\alpha_1 + \alpha_2)\lambda - 1 + \alpha_1 + \alpha_2 = 0$$
$$\lambda^2 - (\alpha_1 - \alpha_2)\lambda + 1 - \alpha_1 - \alpha_2 = 0 \qquad (4.2.4.9)$$

with solutions

$$\lambda_1 = 1, \qquad \lambda_2 = \alpha_1 + \alpha_2 - 1$$

$$\lambda_{3/4} = \frac{\alpha_1 - \alpha_2}{2} \pm \left[\frac{(\alpha_1 - \alpha_2)^2}{4} - 1 + \alpha_1 - \alpha_2\right]^{1/2}. \qquad (4.2.4.10)$$

λ_1 and λ_2 are identical with the solution of the asymmetric case of two kinds of layers [*cf.* equation (4.2.4.6)]. They yield sharp

The final solution of the diffraction problem results in the following general intensity formula:

$$I(\mathbf{H}) = L(h,k)N \sum_\nu \{A_\nu(\mathbf{H})(1 - |\lambda_\nu|^2)$$
$$\times [1 - 2|\lambda_\nu|\cos 2\pi(l - \varphi_\nu) + |\lambda_\nu|^2]^{-1}$$
$$- 2B_\nu(\mathbf{H})|\lambda_\nu|\sin 2\pi(l - \varphi_\nu)$$
$$\times [1 - 2|\lambda_\nu|\cos 2\pi(l - \varphi_\nu) + |\lambda_\nu|^2]^{-1}\}. \qquad (4.2.4.11)$$

Here A_ν and B_ν represent the real and imaginary part of the constants to be calculated with the aid of the boundary conditions of the problem. The first term in equation (4.2.4.11) determines the symmetrical part of a diffuse reflection with respect to the maximum, and is completely responsible for the integrated

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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, 1949a,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

$$l(\mathbf{r}) = l(z) = \sum_{n_3} \delta(z - n_3 c) \qquad (4.2.4.12)$$

is described by one of the Laue equations:

$$G(L) = |L(L)|^2 = \sin^2 \pi NL / \sin^2 \pi L \qquad (4.2.4.13)$$

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:

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

where ξ denotes the correlation length.

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

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

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

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

The Patterson function is:

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

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:

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

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