4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

The correction term may be important in the case of relatively small (1D) domains. As mentioned above, the structure factor of a chain molecule was neglected. The **H** dependence of F_m, of course, obscures the intensity variation of the diffuse layers as described by (4.2.4.47a).

The matrix method developed for the case of planar disorder was adapted to 2D disorder by Scaringe & Ibers (1979). Other models and corresponding expressions for diffuse scattering are developed from specific microscopic models (potentials), *e.g.* in the case of $Hg_{3-\delta}AsF_6$ (Emery & Axe, 1978; Radons *et al.*, 1983), hollandites (Beyeler *et al.*, 1980; Ishii, 1983), iodine chain compounds (Endres *et al.*, 1982) or urea inclusion compounds (Forst *et al.*, 1987).

4.2.4.3.3. *Correlations between different almost collinear chains*

In real cases there are more or less strong correlations between different chains at least within small domains. Deviations from a strict (3D) order of chain-like structural elements are due to several reasons: shape and structure of the chains, varying binding forces, thermodynamical or kinetic considerations.

Many types of disorder occur. (1) Relative shifts parallel to the common axis while projections along this axis give a perfect 2D ordered net ('axial disorder'). (2) Relative fluctuations of the distances between the chains (perpendicular to the unique axis) with short-range order along the transverse **a** and/or **b** directions. The net of projected chains down to the *ab* plane is distorted ('net distortions'). Disorder of types (1) and (2) is sometimes correlated owing to non-uniform cross sections of the chains. (3) Turns, twists and torsions of chains or parts of chains. This azimuthal type of disorder may be treated similarly to the case of azimuthal disorder of single-chain molecules. Correlations between axial shifts and torsions produce 'screw shifts' (helical structures). Torsion of chain parts may be of dynamic origin (rotational vibrations). (4) Tilting or bending of the chains in a uniform or non-uniform way ('conforming/non-conforming'). Many of these types and a variety of combinations between them are found in polymer and liquid crystals and are treated therefore separately. Only some simple basic ideas are discussed here in brief.

For the sake of simplicity the paracrystal concept in combination with Gaussians is used again. Distribution functions are given by convolution products of next-nearest-neighbour distribution functions. As long as averaged lattice directions and lattice constants in a plane perpendicular to the chain axis exist, only two functions $a_{100} = a_1(xyz)$ and $a_{010} = a_2(xyz)$ are needed to describe the arrangement of next-nearest chains. Longitudinal disorder is treated as before by a third distribution function $a_{001} = a_3(xyz)$. The phenomena of chain bending or tilting may be incorporated by an x and y dependence of a_3. Any general fluctuation in the spatial arrangement of chains is given by

$$a_{mpq} = a_1 * \ldots * a_1 * a_2 * \ldots * a_2 * a_3 * \ldots * a_3. \quad (4.2.4.50)$$

(m-fold, p-fold, q-fold self-convolution of a_1, a_2, a_3, respectively.)

$$w(\mathbf{r}) = \delta(\mathbf{r}) \sum_m \sum_p \sum_q [a_{mpq}(\mathbf{r}) + a_{-mpq}(\mathbf{r})]. \quad (4.2.4.51)$$

a_ν ($\nu = 1, 2, 3$) are called fundamental functions. If an averaged lattice cannot be defined, more fundamental functions a_ν are needed to account for correlations between them.

By Fourier transformations the interference function is given by

$$G(\mathbf{H}) = \sum_m \sum_p \sum_q F_1^m F_2^p F_3^q = G_1 G_2 G_3;$$
$$\quad (4.2.4.52)$$
$$G_\nu = \text{Re}\{(1 + |F_\nu|)/(1 - |F_\nu|)\}.$$

If Gaussian functions are assumed, simple pictures are derived. For example:

$$a_1(\mathbf{r} + \langle \mathbf{a} \rangle) = 1/(2\pi)^{3/2} \cdot 1/(\Delta_{11}\Delta_{12}\Delta_{13})$$
$$\times \exp\{-\tfrac{1}{2}[(x^2/\Delta_{11}^2) + (y^2/\Delta_{12}^2) + (z^2/\Delta_{13}^2)]\}$$
$$\quad (4.2.4.53)$$

describes the distribution of neighbours in the x direction (mean distance $\langle a \rangle$). Parameter Δ_{13} concerns axial, Δ_{11} and Δ_{12} radial and tangential fluctuations, respectively. Pure axial distribution along **c** is given by projection of a_1 on the z axis, pure net distortions by projection on the $x - y$ plane. If the chain-like structure is neglected the interference function

$$G_1(\mathbf{H}) = \exp\{-2\pi^2(\Delta_{11}^2 H^2 + \Delta_{12}^2 K^2 + \Delta_{13}^2 L^2)\} \quad (4.2.4.54)$$

describes a set of diffuse planes perpendicular to **a*** with mean distance $1/\langle a \rangle$. These diffuse layers broaden along H with $m\Delta_{11}$ and decrease in intensity along K and L monotonically. There is an ellipsoidal-shaped region in reciprocal space defined by main axes of length $1/\Delta_{11}, 1/\Delta_{12}, 1/\Delta_{13}$ with a limiting surface given by $|F| \simeq 0.1$, beyond which the diffuse intensity is completely smeared out. The influence of a_2 may be discussed in an analogous way.

If the chain-like arrangement parallel to **c** [equation (4.2.4.12)] is taken into consideration,

$$l(z) = \sum_{n_3} \delta(z - n_3 c);$$

the set of planes perpendicular to **a*** (and/or **b***) is subdivided in the L direction by a set of planes located at $l \cdot 1/c$ [equation (4.2.4.15)].

Longitudinal disorder is given by $a_3(z)$ [equation (4.2.4.48), $\Delta_{33} = \Delta$] and leads to two intersecting sets of broadened diffuse layer systems.

Particular cases like pure axial distributions ($\Delta_{11}, \Delta_{12} \sim 0$), pure tangential distributions (net distortions: $\Delta_{11}, \Delta_{13} \sim 0$), uniform bending of chains or combinations of these effects are discussed in the monograph of Vainshtein (1966).

4.2.4.4. *Disorder with three-dimensional correlations (defects, local ordering and clustering)*

4.2.4.4.1. *General formulation (elastic diffuse scattering)*

In this section general formulae for diffuse scattering will be derived which may best be applied to crystals with a well ordered average structure, characterized by (almost) sharp Bragg peaks. Textbooks and review articles concerning defects and local ordering are by Krivoglaz (1969), Dederichs (1973), Peisl (1975), Schwartz & Cohen (1977), Schmatz (1973, 1983), Bauer (1979), and Kitaigorodsky (1984). A series of interesting papers on local order is given by Young (1975) and also by Cowley *et al.* (1979). Expressions for polycrystalline sample material are given by Warren (1969) and Fender (1973).

Two general methods may be applied:

(*a*) the average difference cluster method, where a representative cluster of scattering differences between the average structure and the cluster is used; and

(*b*) the method of short-range-order correlation functions where formal parameters are introduced.

Both methods are equivalent in principle. The cluster method is generally more convenient in cases where a single average cluster is a good approximation. This holds for small concentrations of clusters with sufficient space in between. The method of short-range-order parameters is optimal in cases where isolated clusters are not realized and the correlations do not extend to long distances. Otherwise periodic solutions are more convenient in most cases.

In any case, the first step towards the solution of the diffraction problem is the accurate determination of the average structure. As

described in Section 4.2.3.2 important information on fractional occupations, interstitials and displacements (unusual thermal parameters) of atoms may be derived. Unfortunately all defects contribute to diffuse scattering; hence one has to start with the assumption that the disorder to be interpreted is predominant. Fractional occupancy of certain lattice sites by two or more kinds of atoms plays an important role in the literature, especially in metallic or ionic structures. Since vacancies may be treated as atoms with zero scattering amplitude, structures containing vacancies may be formally treated as multi-component systems.

Since the solution of the diffraction problem should not be restricted to metallic systems with a simple (primitive) structure, we have to consider the structure of the unit cell – as given by the average structure – and the propagation of order according to the translation group separately. In simple metallic systems this difference is immaterial. It is well known that the thermodynamic problem of propagation of order in a three-dimensional crystal can hardly be solved analytically in a general way. Some solutions have been published with the aid of the so-called Ising model using next-nearest-neighbour interactions. They are excellent for an under-standing of the principles of order–disorder phenomena, but they can scarcely be applied quantitatively in practical problems. Hence, methods have been developed to derive the propagation of order from the diffraction pattern by means of Fourier transformation. This method has been described qualitatively in Section 4.2.3.1, and will be used here for a quantitative application. In a first approximation the assumption of a small number of different configurations of the unit cell is made, represented by the corresponding number of structure factors. Displacements of atoms caused by the configurations of the neighbouring cells are excluded. This problem will be treated subsequently.

The finite number of structures of the unit cell in the disordered crystal is given by

$$F_\nu(\mathbf{r}) = \sum_j \sum_\mu \pi_{j\mu}^\nu f_\mu(\mathbf{r} - \mathbf{r}_j). \tag{4.2.4.55}$$

Note that $F_\nu(\mathbf{r})$ is defined in real space, and $\mathbf{r}_j$ gives the position vector of site j; $\pi_{j\mu}^\nu = 1$ if in the νth structure factor the site j is occupied by an atom of kind μ, and 0 elsewhere.

In order to apply the laws of Fourier transformation adequately, it is useful to introduce the distribution function of F_ν

$$\pi_\nu(\mathbf{r}) = \sum_\mathbf{n} \pi_{\mathbf{n}\nu} \delta(\mathbf{r} - \mathbf{n}) \tag{4.2.4.56}$$

with $\pi_{\mathbf{n}\nu} = 1$, if the cell $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ has the F_ν structure, and $\pi_{\mathbf{n}\nu} = 0$ elsewhere.

In the definitions given above $\pi_{\mathbf{n}\nu}$ are numbers (scalars) assigned to the cell. Since all these are occupied we have

$$\sum_\nu \pi_\nu(\mathbf{r}) = l(\mathbf{r})$$

with $l(\mathbf{r}) =$ lattice in real space.

The structure of the disordered crystal is given by

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}). \tag{4.2.4.57}$$

$\pi_\nu(\mathbf{r})$ consists of $\alpha_\nu N$ points, where $N = N_1N_2N_3$ is the total (large) number of unit cells and α_ν denotes the *a priori* probability (concentration) of the νth cell occupation.

It is now useful to introduce

$$\Delta\pi_\nu(\mathbf{r}) = \pi_\nu(\mathbf{r}) - \alpha_\nu l(\mathbf{r}) \tag{4.2.4.58}$$

with

$$\sum_\nu \Delta\pi_\nu(\mathbf{r}) = \sum_\nu \pi_\nu(\mathbf{r}) - l(\mathbf{r})\sum_\nu \alpha_\nu = l(\mathbf{r}) - l(\mathbf{r}) = 0.$$

Introducing (4.2.4.58) into (4.2.4.57):

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r})\sum_\nu \alpha_\nu F_\nu(\mathbf{r})$$

$$= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r})\langle F(\mathbf{r})\rangle. \tag{4.2.4.59}$$

Similarly:

$$\Delta F_\nu(\mathbf{r}) = F_\nu(\mathbf{r}) - \langle F(\mathbf{r})\rangle$$

$$\sum_\nu \alpha_\nu \Delta F_\nu(\mathbf{r}) = \sum_\nu \alpha_\nu F_\nu(\mathbf{r}) - \sum_\nu \alpha_\nu \langle F(\mathbf{r})\rangle = 0. \tag{4.2.4.60}$$

Using (4.2.4.60) it follows from (4.2.4.58) that

$$\sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r})$$

$$+ \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \langle F(\mathbf{r})\rangle + l(\mathbf{r}) * \langle F(\mathbf{r})\rangle$$

$$= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) + l(\mathbf{r}) * \langle F(\mathbf{r})\rangle. \tag{4.2.4.61}$$

Comparison with (4.2.4.59) yields

$$\sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) = \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}).$$

Fourier transformation of (4.2.4.61) gives

$$\sum_\nu \Pi_\nu(\mathbf{H})F_\nu(\mathbf{H}) = \sum_\nu \Delta\Pi_\nu(\mathbf{H})\Delta F_\nu(\mathbf{H}) + L(\mathbf{H})\langle F(\mathbf{H})\rangle$$

with

$$\sum_\nu \Delta\Pi_\nu(\mathbf{H}) = 0; \quad \sum_\nu \Delta F_\nu(\mathbf{H}) = 0.$$

The expression for the scattered intensity is therefore

$$I(\mathbf{H}) = \left|\sum_\nu \Delta\Pi_\nu(\mathbf{H})\Delta F_\nu(\mathbf{H})\right|^2 + |L(\mathbf{H})\langle F(\mathbf{H})\rangle|^2$$

$$+ L(\mathbf{H})\left\{\langle F^+(\mathbf{H})\rangle \sum_\nu \Delta\Pi_\nu(\mathbf{H})F_\nu(\mathbf{H})\right.$$

$$\left. + \langle F^+(\mathbf{H})\rangle \sum_\nu \Delta\Pi_\nu^+(\mathbf{H})F_\nu^+(\mathbf{H})\right\}. \tag{4.2.4.62}$$

Because of the multiplication by $L(\mathbf{H})$ the third term in (4.2.4.62) contributes to sharp reflections only. Since they are correctly given by the second term in (4.2.4.62), the third term vanishes, Hence, the diffuse part is given by

$$I_d(\mathbf{H}) = \left|\sum_\nu \Delta\Pi_\nu(\mathbf{H})\Delta F_\nu(\mathbf{H})\right|^2. \tag{4.2.4.63}$$

For a better understanding of the behaviour of diffuse scattering it is useful to return to real space:

$$i_d(\mathbf{r}) = \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \sum_{\nu'} \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= \sum_\nu \sum_{\nu'} \Delta\pi_\nu(\mathbf{r}) * \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) \tag{4.2.4.64}$$

and with (4.2.4.58):

$$i_d(\mathbf{r}) = \sum_\nu \sum_{\nu'} [\pi_\nu(\mathbf{r}) - \alpha_\nu l(\mathbf{r})] * [\pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \qquad (4.2.4.65)$$

Evaluation of this equation for a single term yields

$$[\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_\nu l(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r})$$

$$- \alpha_{\nu'} l(\mathbf{r}) * \pi_\nu(\mathbf{r}) + \alpha_\nu \alpha_{\nu'} l(\mathbf{r}) * l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(\mathbf{r}). \qquad (4.2.4.66)$$

Since $l(\mathbf{r})$ is a periodic function of points, all convolution products with $l(\mathbf{r})$ are also periodic. For the final evaluation the decrease of a number of overlapping points (maximum N) in the convolution products with increasing displacements of the functions is neglected (no particle-size effect). Then (4.2.4.66) becomes

$$[\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N\alpha_\nu \alpha_{\nu'} l(\mathbf{r}) - N\alpha_\nu \alpha_{\nu'} l(\mathbf{r}) + N\alpha_\nu \alpha_{\nu'} l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= [\pi_\nu(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N\alpha_\nu \alpha_{\nu'} l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \qquad (4.2.4.67)$$

If the first term in (4.2.4.67) is considered, the convolution of the two functions for a given distance $\mathbf{n}$ counts the number of coincidences of the function $\pi_\nu(\mathbf{r})$ with $\pi_{\nu'}(-\mathbf{r})$. This quantity is given by $Nl(\mathbf{r})\alpha_\nu p_{\nu\nu'}(-\mathbf{r})$, where $\alpha_\nu p_{\nu\nu'}(\mathbf{r})$ is the probability of a pair occupation in the $\mathbf{r}$ direction.

Equation (4.2.4.67) then reads:

$$[Nl(\mathbf{r})\alpha_\nu p_{\nu\nu'}(-\mathbf{r}) - N\alpha_\nu \alpha_{\nu'} l(\mathbf{r})]$$

$$* \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})$$

$$= N\alpha_\nu [p'_{\nu\nu'}(-\mathbf{r}) l(\mathbf{r})]$$

$$* [\Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \qquad (4.2.4.68)$$

with $p'_{\nu\nu'}(\mathbf{r}) = p_{\nu\nu'}(\mathbf{r}) - \alpha_{\nu'}$. The function $\alpha_\nu p'_{\nu\nu'}(\mathbf{r})$ is usually called the pair-correlation function $g \leftrightarrow \alpha_{\nu\nu'|\mathbf{nn'}}$ in the physical literature.

The following relations hold:

$$\sum_\nu \alpha_\nu = 1 \qquad (4.2.4.69a)$$

$$\sum_{\nu'} \alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'}; \quad \sum_{\nu'} \alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = 0 \qquad (4.2.4.69b)$$

$$\sum_\nu \alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_\nu; \quad \sum_\nu \alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = 0 \qquad (4.2.4.69c)$$

$$\alpha_\nu p_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'} p_{\nu'\nu}(-\mathbf{r}). \qquad (4.2.4.69d)$$

Also, functions normalized to unity are in use. Obviously the following relation is valid: $p'_{\nu\nu'}(0) = \delta_{\nu\nu'} - \alpha_{\nu'}$.
Hence:

$$\alpha_{\nu\nu'|\mathbf{nn'}} = \alpha_\nu p'_{\nu\nu'}(\mathbf{r})/(\delta_{\nu\nu'} - \alpha_{\nu'})$$

is unity for $\mathbf{r} = 0$ ($\mathbf{n} = \mathbf{n'}$). This property is especially convenient in binary systems.

With (4.2.4.68), equation (4.2.4.64) becomes

$$i_d(\mathbf{r}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu p'_{\nu\nu'}(-\mathbf{r}) l(\mathbf{r})] * [\Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})]$$

$$(4.2.4.70)$$

and Fourier transformation yields

$$I_d(\mathbf{H}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \Delta F_\nu(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}).$$

$$(4.2.4.71)$$

It may be concluded from equations (4.2.4.69) that all functions $p'_{\nu\nu'}(\mathbf{r})$ may be expressed by $p'_{11}(\mathbf{r})$ in the case of two structure factors F_1, F_2. Then all $p'_{\nu\nu'}(\mathbf{r})$ are symmetric in $\mathbf{r}$; the same is true for the $P'_{\nu\nu'}(\mathbf{H})$. Consequently, the diffuse reflections described by (4.2.4.71) are all symmetric. The position of the diffuse peak depends strongly on the behaviour of $p'_{\nu\nu'}(\mathbf{r})$; in the case of cluster formation Bragg peaks and diffuse peaks coincide. Diffuse superstructure reflections are observed if the $p'_{\nu\nu'}(\mathbf{r})$ show some damped periodicities.

It should be emphasized that the condition $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ may be violated for $\nu \neq \nu'$ if more than two cell occupations are involved. As shown below, the possibly asymmetric functions may be split into symmetric and antisymmetric parts. From equation (4.2.3.8) it follows that the Fourier transform of the antisymmetric part of $p'_{\nu\nu'}(\mathbf{r})$ is also antisymmetric. Hence, the convolution in the two terms in square brackets in (4.2.4.71) yields an antisymmetric contribution to each diffuse peak, generated by the convolution with the reciprocal lattice $L(\mathbf{h})$.

Obviously, equation (4.2.4.71) may also be applied to primitive lattices, occupied by two or more kinds of atoms. Then the structure factors F_ν are merely replaced by the atomic scattering factors f_ν and the α_ν are equivalent to the concentrations of atoms c_ν. In terms of the $\alpha_{\nu\nu'|\mathbf{nn'}}$ (Warren short-range-order parameters) equation (4.2.4.71) reads

$$I_d(\mathbf{H}) = N(\overline{f^2} - \bar{f}^2) \sum_\mathbf{n} \sum_{\mathbf{n'}} \alpha_{\nu\nu'|\mathbf{nn'}} \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n'})\}.$$

$$(4.2.4.71a)$$

In the simplest case of a binary system A, B

$$\alpha_{\mathbf{nn'}} = (1 - p_{AB|\mathbf{nn'}})/c_B = (1 - p_{BA|\mathbf{nn'}})/c_A;$$

$$c_A p_{AB} = c_B p_{BA}; \quad p_{AA} = 1 - p_{AB};$$

$$I_d(\mathbf{H}) = N c_A c_B (f_A - f_B)^2 \sum_\mathbf{n} \sum_{\mathbf{n'}} \alpha_{\mathbf{nn'}}$$

$$\times \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n'})\}. \qquad (4.2.4.71b)$$

[The exponential in (4.2.4.71b) may even be replaced by a cosine term owing to the centrosymmetry of this particular case.]

It should be mentioned that the formulations of the problem in terms of pair probabilities, pair correlation functions, short-range-order parameters or concentration waves (Krivoglaz, 1969) are equivalent. Using continuous electron (or nuclear) density functions where site occupancies are implied, the Patterson function may be used, too (Cowley, 1981).

4.2.4.4.2. *Random distribution*

As shown above in the case of random distributions all $p'_{\nu\nu'}(\mathbf{r})$ are zero, except for $\mathbf{r} = 0$. Consequently, $p'_{\nu\nu'}(\mathbf{r}) l(\mathbf{r})$ may be replaced by

$$\alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = \alpha_\nu \delta_{\nu\nu'} - \alpha_\nu \alpha_{\nu'}. \qquad (4.2.4.72)$$

According to (4.2.4.59) and (4.2.4.61) the diffuse scattering can be given by the Fourier transformation of

$$\sum_\nu \sum_{\nu'} \Delta \pi_\nu(\mathbf{r}) * \Delta \pi_{\nu'}(-\mathbf{r}) * F_\nu(\mathbf{r}) * F_{\nu'}(-\mathbf{r})$$

$$= \sum_\nu \sum_{\nu'} p'_{\nu\nu'}(\mathbf{r}) * F_\nu(\mathbf{r}) * F_{\nu'}(-\mathbf{r})$$

or with (4.2.4.72):

$$i_d(\mathbf{r}) = N \sum_\nu \sum_{\nu'} [\alpha_\nu \delta_{\nu\nu'} - \alpha_\nu \alpha_{\nu'}] * F_\nu(\mathbf{r}) * F_{\nu'}(-\mathbf{r}).$$

Fourier transformation gives

$$I_d(\mathbf{H}) = N \left\{ \sum_\nu \alpha_\nu |F_\nu(\mathbf{H})|^2 - \sum_\nu \alpha_\nu F_\nu(\mathbf{H}) \sum_{\nu'} \alpha_{\nu'} F_{\nu'}^+(\mathbf{H}) \right\}$$

$$= N\{ \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \}. \qquad (4.2.4.73)$$

This is the most general form of any diffuse scattering of systems ordered randomly ('Laue scattering'). Occasionally it is called 'incoherent scattering' (see Section 4.2.2).

4.2.4.4.3. *Short-range order in multi-component systems*

The diffuse scattering of a disordered binary system without displacements of the atoms has already been discussed in Section 4.2.4.4.1. It could be shown that all distribution functions $p'_{\nu\nu'}(\mathbf{r})$ are mutually dependent and may be replaced by a single function [*cf.* (4.2.4.69)]. In that case $p'_{\nu\nu'}(\mathbf{r}) = p'_{\nu\nu'}(-\mathbf{r})$ was valid for all. This condition, however, may be violated in multi-component systems. If a tendency towards an $F_1F_2F_3$ order in a ternary system is assumed, for example, $p_{12}(\mathbf{r})$ is apparently different from $p_{12}(-\mathbf{r})$. In this particular case it is useful to introduce

$$\langle p'_{\nu\nu'}(\mathbf{r}) \rangle = \tfrac{1}{2}[p'_{\nu\nu'}(\mathbf{r}) + p'_{\nu\nu'}(-\mathbf{r})];$$

$$\Delta p'_{\nu\nu'}(\mathbf{r}) = \tfrac{1}{2}[p'_{\nu\nu'}(\mathbf{r}) - p'_{\nu\nu'}(-\mathbf{r})]$$

and their Fourier transforms $\langle P'_{\nu\nu'}(\mathbf{H}) \rangle, \Delta P'_{\nu\nu'}(\mathbf{H})$, respectively.

The asymmetric correlation functions are therefore expressed by

$$p'_{\nu\nu'}(\mathbf{r}) = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle + \Delta p'_{\nu\nu'}(\mathbf{r});$$

$$p'_{\nu\nu'}(-\mathbf{r}) = \langle p'_{\nu\nu'}(\mathbf{r}) \rangle - \Delta p'_{\nu\nu'}(\mathbf{r});$$

$$\Delta p'_{\nu\nu}(\mathbf{r}) = 0.$$

Consequently, $i_d(\mathbf{r})$ (4.2.4.70) and $I_d(\mathbf{H})$ (4.2.4.71) may be separated according to the symmetric and antisymmetric contributions. The final result is:

$$I_d(\mathbf{H}) = N \left\{ \sum_\nu \alpha_\nu [P'_{\nu\nu}(\mathbf{H}) * L(\mathbf{H})] |F_\nu(\mathbf{H})|^2 \right.$$

$$+ \sum_{\nu > \nu'} \alpha_\nu [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle * L(\mathbf{H})]$$

$$\times [\Delta F_\nu(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) + \Delta F_\nu^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})]$$

$$+ \sum_{\nu > \nu'} \alpha_\nu [\Delta P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})]$$

$$\left. \times [\Delta F_\nu(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) - \Delta F_\nu^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})] \right\}. \qquad (4.2.4.74)$$

Obviously, antisymmetric contributions to line profiles will only occur if structure factors of acentric cell occupations are involved. This important property may be used to draw conclusions with respect to structure factors involved in the statistics. It should be mentioned here that the Fourier transform of the antisymmetric function $\Delta p'_{\nu\nu'}(\mathbf{r})$ is imaginary and antisymmetric. Since the last term in (4.2.4.74) is also imaginary, the product of the two factors in brackets is real, as it should be.

4.2.4.4.4. *Displacements: general remarks*

Even small displacements may have an important influence on the problem of propagation of order. Therefore, no structural treatments other than the introduction of formal parameters (*e.g.* Landau's theory) have been published in the literature. Most of the examples with really reliable results refer to binary systems, and even these represent very crude approximations, as will be shown below. For this reason we shall restrict ourselves here to binary systems, although general formulae where displacements are included may be developed in a formal way.

Two kinds of atoms, $f_1(\mathbf{r})$ and $f_2(\mathbf{r})$, are considered. Obviously, the position of any given atom is determined by its surroundings. Their extension depends on the forces acting on the atom under consideration. These may be very weak in the case of metals (repulsive forces, so-called 'size effect'), but long-range effects have to be expected in ionic crystals. For the development of formulae authors have assumed that small displacements $\Delta_{\nu\nu'}(\mathbf{r})$ may be assigned to the pair correlation functions $p'_{\nu\nu'}(\mathbf{r})$ by adding a phase factor $\exp\{2\pi i\mathbf{H} \cdot \Delta_{\nu\nu'}\mathbf{r}\}$ which is then expanded in the usual way:

$$\exp\{2\pi i\mathbf{H} \cdot \Delta_{\nu\nu'}\mathbf{r}\} \simeq 1 + 2\pi i\mathbf{H} \cdot \Delta_{\nu\nu'}\mathbf{r} - 2[\pi\mathbf{H} \cdot \Delta_{\nu\nu'}\mathbf{r}]^2. \qquad (4.2.4.75)$$

The displacements and correlation probabilities are separable if the change of atomic scattering factors in the angular range considered may be neglected. The formulae in use are given in the next section. As shown below, this method represents nothing other than a kind of average over certain sets of displacements. For this purpose the correct solution of the problem has to be discussed. In the simplest model the displacements are due to next-nearest neighbours only. It is assumed further that the configurations rather than the displacements determine the position of the central atom and a general displacement of the centre of the first shell does not occur (no influence of a strain field). Obviously, the formal correlation function of pairs is not independent of displacements. This difficulty may be avoided either by assuming that the pair correlation function has already been separated from the diffraction data, or by theoretical calculations of the correlation function (mean-field method) (Moss, 1966; de Fontaine, 1972, 1973). The validity of this procedure is subject to the condition that the displacements have no influence on the correlation functions themselves.

The observation of a periodic average structure justifies the definition of a periodic array of origins which normally depends on the degree of order. Local deviations of origins may be due to fluctuations in the degree of order and due to the surrounding atoms of a given site occupation. For example, a b.c.c. lattice with eight nearest neighbours is considered. It is assumed that only these have an influence on the position of the central atom owing to different forces of the various configurations. With two kinds of atoms, there are $2^9 = 512$ possible configurations of the cluster (central atom plus 8 neighbours). Symmetry considerations reduce this number to 28. Each is characterized by a displacement vector. Hence, their *a priori* probabilities and the propagation of 28 different configurations have to be determined. Since each atom has to be considered as the centre once, this problem may be treated by introducing 28 different atomic scattering factors as determined from the displacements: $f_\nu(\mathbf{r}) \exp\{2\pi i\mathbf{H} \cdot \Delta\mathbf{r}_{\nu\nu'}\}$. The diffraction problem has to be solved with the aid of the propagation of order of overlapping clusters. This is demonstrated by a two-dimensional model with four nearest neighbours (Fig. 4.2.4.1). Here the central and the neighbouring cluster (full and broken lines) overlap with two sites in the, *e.g.*, **x** direction. Hence, only neighbouring clusters with the same overlapping pairs are admitted. These restrictions introduce severe difficulties into the problem of propagation of cluster ordering which determines the displacement field. Since it was assumed that the problem of pair correlation had been solved, the cluster probabilities may be derived by calculating

$$\alpha_\nu l(\mathbf{r}) \prod_{\mathbf{n} \neq 0} p'_{\nu\nu'}(\mathbf{r} - \mathbf{n}). \qquad (4.2.4.76)$$
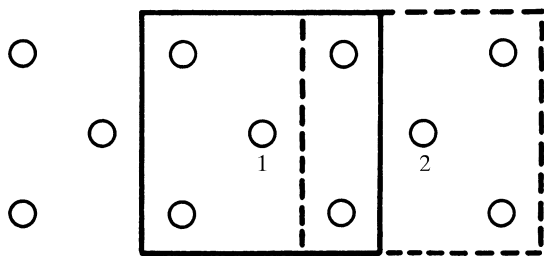
432

Fig. 4.2.4.1. Construction of the correlation function in the method of overlapping clusters.

In the product only next-nearest neighbours have to be included. This must be performed for the central cluster $(\mathbf{r} = 0)$ *and* for the reference cluster at $\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, because all are characterized by different displacements. So far, possible displacement of the centre has not been considered; this may also be influenced by the problem of propagation of cluster ordering. These displacement factors should best be attached to the function describing the propagation of order which determines, in principle, the local fluctuations of the lattice constants (strain field *etc.*). This may be understood by considering a binary system with a high degree of order but with atoms of different size. Large fluctuations of lattice constants are involved in the case of exsolution of the two components because of their different lattice parameters, but they become small in the case of superstructure formation where a description in terms of antiphase domains is reasonable (equal lattice constants). This example demonstrates the mutual dependence of ordering and displacements which is mostly neglected in the literature.

The method of assigning phase factors to the pair correlation function is now discussed. Pair correlation functions average over all pairs of clusters having the same central atom. An analogous argument holds for displacements: using pair correlations for the determination of displacements means nothing other than averaging over all displacements caused by various clusters around the same central atom. There remains the general strain field due to the propagation of order, whereas actual displacements of atoms are realized by fluctuations of configurations. Since large fluctuations of this type occur in highly disordered crystals, the displacements become increasingly irrelevant. Hence, the formal addition of displacement factors to the pair correlation function does not yield too much information about the structural basis of the displacements. This situation corresponds exactly to the relationship between a Patterson function and a real structure: the structure has to be found which explains the more or less complicated function completely, and its unique solution is rather difficult. These statements seem to be necessary because in most publications related to this subject these considerations are not taken into account adequately. Displacements usually give rise to antisymmetric contributions to diffuse reflections. As pointed out above, the influence of displacements has to be considered as phase factors which may be attached either to the structure factors or to the Fourier transforms $P'_{\nu\nu'}(\mathbf{H})$ of the correlation functions in equation (4.2.4.71). As has been mentioned in the context of equation (4.2.4.74) antisymmetric contributions will occur if acentric structure factors are involved. Apparently, this condition is met by the phase factors of displacements. In consequence, antisymmetric contributions to diffuse reflections may also originate from the displacements. This fact can also be demonstrated if the assignment of phase factors to the Fourier transforms of the correlation functions is advantageous. In this case equations (4.2.4.69a,b) are no longer valid because the functions $p'_{\nu\nu'}(\mathbf{r})$ become complex. The most important change is the relation corresponding to (4.2.4.69):

$$\alpha_\nu p'_{\nu\nu'}(\mathbf{r}) = \alpha_{\nu'}p'^+_{\nu\nu'}(-\mathbf{r}) \leftrightarrow \alpha_{\nu'}P'_{\nu\nu'}(\mathbf{H}) = \alpha_{\nu'}P'^+_{\nu}(\mathbf{H}). \quad (4.2.4.77)$$

Strictly speaking we have to replace the *a priori* probabilities α_ν by complex numbers $\alpha_\nu \exp(2\pi i \Delta\mathbf{r}_\nu \cdot \mathbf{H})$ which are determined by the position of the central atom. In this way all correlations between displacements may be included with the aid of the clusters mentioned above. To a rough approximation it may be assumed that no correlations of this kind exist. In this case the complex factors may be assigned to the structure factors involved. Averaging over all displacements results in diffraction effects which are very similar to a static Debye–Waller factor for all structure factors. On the other hand, the thermal motion of atoms is treated similarly. Obviously both factors affect the sharp Bragg peaks. Hence, this factor can easily be determined by the average structure which contains a Debye–Waller factor including static and thermal displacements. It should be pointed out, however, that these static displacements cause elastic diffuse scattering which cannot be separated by inelastic neutron scattering techniques.

A careful study of the real and imaginary parts of

$$\langle p'_{\nu\nu'}(\mathbf{r})\rangle = \langle p'_{\nu\nu'}(\mathbf{r})\rangle_R + \langle p'_{\nu\nu'}(\mathbf{r})\rangle_I$$

and

$$\Delta p'_{\nu\nu'}(\mathbf{r}) = \Delta p'_{\nu\nu'}(\mathbf{r})_R + \Delta p'_{\nu\nu'}(\mathbf{r})_I$$

and their Fourier transforms results, after some calculations, in the following relation for diffuse scattering:

$$
\begin{aligned}
I_d \simeq &\ N \sum_\nu \alpha_\nu |\Delta F_\nu(\mathbf{H})|^2 \{[\langle P'_{\nu\nu}(\mathbf{H})\rangle - \Delta P'_{\nu\nu}(\mathbf{H})] * L(\mathbf{H})\} \\
&+ 2N \sum_{\nu>\nu'} \alpha_\nu (\Delta F_\nu \Delta F^+_{\nu'})_R \\
&\times \{[\langle P'_{\nu\nu'}(\mathbf{H})\rangle_R - \Delta P'_{\nu\nu'}(\mathbf{H})_I] * L(\mathbf{H})\} \\
&+ 2N \sum_{\nu>\nu'} \alpha_\nu (\Delta F_\nu \Delta F^+_{\nu'})_I \\
&\times \{[\langle P'_{\nu\nu'}(\mathbf{H})\rangle_I - \Delta P'_{\nu\nu'}(\mathbf{H})_R] * L(\mathbf{H})\}. \quad (4.2.4.78)
\end{aligned}
$$

It should be noted that all contributions are real. This follows from the properties of Fourier transforms of symmetric and antisymmetric functions. All $\Delta P_{\nu\nu'}(\mathbf{H})$ are antisymmetric; hence they generate antisymmetric contributions to the line profiles. In contrast to equation (4.2.4.75), the real *and* the imaginary parts of the structure factors contribute to the asymmetry of the line profiles.

4.2.4.4.5. *Distortions in binary systems*

In substitutional binary systems (primitive cell with only one sublattice) the Borie–Sparks method is widely used (Sparks & Borie, 1966; Borie & Sparks, 1971). The method is formulated in the short-range-order-parameter formalism. The diffuse scattering may be separated into two parts (*a*) owing to short-range order and (*b*) owing to static displacements.

Corresponding to the expansion (4.2.4.75), $I_d = I_{\text{sro}} + I_2 + I_3$, where I_{sro} is given by equation (4.2.4.71*b*) and the correction terms I_2 and I_3 relate to the linear and the quadratic term in (4.2.4.75). The intensity expression will be split into terms of A–A, A–B, . . . pairs. More explicitly $\Delta_{\nu\nu'}\mathbf{r} = \mathbf{u}_{\mathbf{n}\nu} - \mathbf{u}_{\mathbf{n}'\nu'}$ and with the following abbreviations:

$$
\begin{aligned}
\delta_{\mathbf{nn'}|AA} &= \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|A} = x_{\mathbf{nn'}|AA}\mathbf{a} + y_{\mathbf{nn'}|AA}\mathbf{b} + z_{\mathbf{nn'}|AA}\mathbf{c} \\
\delta_{\mathbf{nn'}|AB} &= \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|B} = \ldots \\
F_{\mathbf{nn'}|AA} &= f_A^2/(f_A - f_B)^2 \cdot [(c_A/c_B) + \alpha_{\mathbf{nn'}}] \\
F_{\mathbf{nn'}|BB} &= f_B^2/(f_A - f_B)^2 \cdot [(c_B/c_A) + \alpha_{\mathbf{nn'}}] \\
F_{\mathbf{nn'}|AB} &= 2f_A f_B/(f_A - f_B)^2 \cdot (1 - \alpha_{\mathbf{nn'}}) = F_{\mathbf{nn'}|BA}
\end{aligned}
$$

one finds (where the short-hand notation is self-explanatory):

$$I_2 = 2\pi i c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{H \cdot [F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA} \rangle$$

$$+ F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB} \rangle] + K \cdot [\text{`}y\text{'}]$$

$$+ L \cdot [\text{`}z\text{'}]\} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \qquad (4.2.4.79)$$

$$I_3 = c_A c_B (f_A - f_B)^2 (-2\pi)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{H^2 [F_{\mathbf{nn}'} \langle x_{\mathbf{nn}'|AA}^2 \rangle$$

$$+ F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB}^2 \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB}^2 \rangle]$$

$$+ K^2 \cdot [\text{`}y^2\text{'}] + L^2 \cdot [\text{`}z^2\text{'}]$$

$$+ HK [F_{\mathbf{nn}'|AA} \langle (xy)_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle (xy)_{\mathbf{nn}'|BB} \rangle$$

$$+ F_{\mathbf{nn}'|AB} \langle (xy)_{\mathbf{nn}'|AB} \rangle]$$

$$+ KL[\text{`}(yz)\text{'}] + LH[\text{`}(zx)\text{'}]\}$$

$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}. \qquad (4.2.4.80)$$

With further abbreviations

$$\gamma_{\mathbf{nn}'|x} = 2\pi (F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB} \rangle$$

$$+ F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB} \rangle)$$

$$\gamma_{\mathbf{nn}'|y} = \cdots$$

$$\gamma_{\mathbf{nn}'|z} = \cdots$$

$$\delta_{\mathbf{nn}'|x} = (-2\pi^2)(F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA}^2 \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB}^2 \rangle$$

$$+ F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB}^2 \rangle)$$

$$\delta_{\mathbf{nn}'|y} = \cdots$$

$$\delta_{\mathbf{nn}'|z} = \cdots$$

$$\varepsilon_{\mathbf{nn}'|xy} = (-4\pi^2)(F_{\mathbf{nn}'|AA} \langle (xy)_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle (xy)_{\mathbf{nn}'|BB} \rangle$$

$$+ F_{\mathbf{nn}'|AB} \langle (xy)_{\mathbf{nn}'|AB} \rangle)$$

$$\varepsilon_{\mathbf{nn}'|yz} = \cdots$$

$$\varepsilon_{\mathbf{nn}'|zx} = \cdots$$

$$I_2 = c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i(\gamma_{\mathbf{nn}'|x} + \gamma_{\mathbf{nn}'|y} + \gamma_{\mathbf{nn}'|z})$$

$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}$$

$$I_3 = c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} (\delta_{\mathbf{nn}'|x} H^2 + \delta_{\mathbf{nn}'|y} K^2$$

$$+ \delta_{\mathbf{nn}'|z} L^2 + \varepsilon_{\mathbf{nn}'|xy} HK + \varepsilon_{\mathbf{nn}'|yz} KL$$

$$+ \varepsilon_{\mathbf{nn}'|zx} LH \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}.$$

If the $F_{\mathbf{nn}'|AA}, \dots$ are independent of $|\mathbf{H}|$ in the range of measurement which is better fulfilled with neutrons than with X-rays (see below), $\gamma, \delta, \varepsilon$ are the coefficients of the Fourier series:

$$Q_x = \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i \gamma_{\mathbf{nn}'|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\};$$

$$Q_y = \cdots; \qquad Q_z = \cdots;$$

$$R_x = \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \delta_{\mathbf{nn}'|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\};$$

$$R_y = \cdots; \qquad R_z = \cdots;$$

$$S_{xy} = \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \varepsilon_{\mathbf{nn}'|xy} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\};$$

$$S_{yz} = \cdots; \qquad S_{zx} = \cdots.$$

The functions Q, R, S are then periodic in reciprocal space.

The double sums over $\mathbf{n}, \mathbf{n}'$ may be replaced by $N \sum_{m, n, p}$ where m, n, p are the coordinates of the interatomic vectors $(\mathbf{n} - \mathbf{n}')$ and I_2 becomes

$$I_2 = -N c_A c_B (f_A - f_B)^2 \sum_m \sum_n \sum_p (H \gamma_{lmn|x} + \dots + \dots)$$

$$\times \sin 2\pi (Hm + Kn + Lp). \qquad (4.2.4.81)$$

The intensity is therefore modulated sinusoidally and increases with scattering angle. The modulation gives rise to an asymmetry in the intensity around a Bragg peak. Similar considerations for I_3 reveal an intensity contribution h_i^2 times a sum over cosine terms which is symmetric around the Bragg peaks. This term shows quite an analogous influence of local static displacements and thermal movements: an increase of diffuse intensity around the Bragg peaks and a reduction of Bragg intensities, which is not discussed here. The second contribution I_2 has no analogue owing to the non-vanishing average displacement. The various diffuse intensity contributions may be separated by symmetry considerations. Once they are separated, the single coefficients may be determined by Fourier inversion. Owing to the symmetry constraints there are relations between the displacements $\langle x \dots \rangle$ and, in turn, between the γ and Q components. The same is true for the δ, ε, and R, S components. Consequently, there are symmetry conditions for the individual contributions of the diffuse intensity which may be used to distinguish them. Generally the total diffuse intensity may be split into only a few independent terms. The single components of Q, R, S may be expressed separately by combinations of diffuse intensities which are measured in definite selected volumes in reciprocal space. Only a minimum volume must be explored in order to reveal the behaviour over the whole reciprocal space. This minimum repeat volume is different for the single components: I_{sro}, Q, R, S or combinations of them.

The Borie–Sparks method has been applied very frequently to binary and even ternary systems; some improvements have been communicated by Bardhan & Cohen (1976). The diffuse scattering of the historically important metallic compound Cu_3Au has been studied by Cowley (1950a,b), and the pair correlation parameters could be determined. The typical fourfold splitting was found by Moss (1966) and explained in terms of atomic displacements. The same splitting has been found for many similar compounds such as Cu_3Pd (Ohshima et al., 1976), Au_3Cu (Bessière et al., 1983), and $Ag_{1-x}Mg_x$ ($x = 0.15 - 0.20$) (Ohshima & Harada, 1986). Similar pair correlation functions have been determined. In order to demonstrate the disorder parameters in terms of structural models, computer programs were used (e.g. Gehlen & Cohen, 1965). A similar microdomain model was proposed by Hashimoto (1974, 1981, 1983, 1987). According to approximations made in the theoretical derivation the evaluation of diffuse scattering is generally restricted to an area in reciprocal space where the influence of displacements is of the same order of magnitude as that of the pair correlation function. The agreement between calculation and measurement is fairly good but it should be remembered that the amount and quality of the experimental information used is low. No residual factors are so far available; these would give an idea of the reliability of the results.

The more general case of a multi-component system with several atoms per lattice point was treated similarly by Hayakawa & Cohen (1975). Sources of error in the determination of the short-range-order coefficients are discussed by Gragg et al. (1973). In general the assumption of constant $F_{\mathbf{nn}'|AA}, \dots$ produces an incomplete separation of the order- and displacement-dependent components of diffuse scattering. By an alternative method, by separation of the form factors from the Q, R, S functions and solving a large array of linear relationships by least-squares methods, the accuracy of the separation of the various contributions is improved (Tibbals, 1975;

Georgopoulos & Cohen, 1977; Wu *et al.*, 1983). The method does not work for neutron diffraction. Also, the case of planar short-range order with corresponding diffuse intensity along rods in reciprocal space may be treated along the Borie & Sparks method (Ohshima & Moss, 1983).

Multi-wavelength methods taking advantage of the variation of the structure factor near an absorption edge (anomalous dispersion) are discussed by Cenedese *et al.* (1984). The same authors show that in some cases the neutron method allows for a contrast variation by using samples with different isotope substitution.

4.2.4.4.6. *Powder diffraction*

Evaluation of diffuse-scattering data from powder diffraction follows the same theoretical formulae developed for the determination of the radial distribution function for glasses and liquids (Debye & Menke, 1931; Warren & Gingrich, 1934). The final formula for random distributions may be given as (Fender, 1973)

$$I_d^p = \{\langle|F(\mathbf{H})|^2\rangle - |\langle F(\mathbf{H})\rangle|^2\} \sum_i s_i \sin(2\pi Hr_i)/(2\pi Hr_i).$$

$$(4.2.4.82)$$

s_i represents the number of atoms at distance r_i from the origin. An equivalent expression for a substitutional binary alloy is

$$I_d^p = \alpha(1-\alpha)\{|f_2(\mathbf{H}) - f_2(\mathbf{H})|^2\} \sum_i s_i \sin(2\pi Hr_i)/(2\pi Hr_i).$$

$$(4.2.4.83)$$

4.2.4.4.7. *Small concentrations of defects*

In the literature small concentrations are treated in terms of fluctuations of the functions $\pi_{\mathbf{n}\nu}$ as defined in equation (4.2.4.56). Generally we prefer the introduction of the distribution function of the defects or clusters. Since this problem has already been treated in Section 4.2.4.4.3 only some very brief remarks are given here. The most convenient way to derive the distribution function correctly from experimental data is the use of low-angle scattering which generally shows one or more clear maxima caused by partly periodic properties of the distribution function. For the deconvolution of the distribution function, received by Fourier transformation of the corrected diffused low-angle scattering, the reader is referred to the relevant literature. Since deconvolutions are not unique some reasonable assumptions are necessary for the final solution. Anomalous scattering may be very helpful if applicable.

4.2.4.4.8. *Cluster method*

As mentioned above, the cluster method may be useful for the interpretation of disorder problems. In the general formula of diffuse scattering of random distributions equation (4.2.2.13) may be used. Here $|\langle F(\mathbf{H})\rangle|^2$ describes the sharp Bragg maxima, while $|\Delta F(\mathbf{H})|^2 = \langle|F(\mathbf{H})|^2\rangle - |\langle F(\mathbf{H})\rangle|^2$ represents the contribution to diffuse scattering. Correlation effects can also be taken into account by using clusters of sufficient size if their distribution may be considered as random in good approximation. The diffuse intensity is then given by

$$I_d(\mathbf{H}) = \sum_\nu p_\nu |F_\nu(\mathbf{H})|^2 - |\sum_\nu p_\nu F_\nu(\mathbf{H})|^2, \qquad (4.2.4.84)$$

where $F_\nu(\mathbf{H})$ represents the difference structure factor of the νth cluster and p_ν is its *a priori* probability. Obviously equation (4.2.4.84) is of some use in two cases only. (1) The number of clusters is sufficiently small and meets the condition of nearly random distribution. In principle, its structure may then be determined with the aid of refinement methods according to

equation (4.2.4.84). Since the second term is assumed to be known from the average structure, the first term may be evaluated by introducing as many parameters as there are clusters involved. A special computer program for incoherent refinement has to be used if more than one representative cluster has to be introduced. In the case of more clusters, constraints are necessary. (2) The number of clusters with similar structures is not limited. It may be assumed that their size distribution may be expressed by well known analytical expressions, *e.g.* Gaussians or Lorentzians. The distribution is still assumed to be random.

An early application of the cluster method was the calculation of the diffuse intensity of Guinier–Preston zones, where a single cluster is sufficient (see, *e.g.*, Gerold, 1954; Bubeck & Gerold, 1984). Unfortunately no refinements of cluster structures have so far been published. The full theory of the cluster method was outlined by Jagodzinski & Haefner (1967).

Some remarks on the use of residual factors should be added here. Obviously the diffuse scattering may be used for refinements in a similar way as in conventional structure determination. For this purpose a sufficiently small reciprocal lattice has to be defined. The size of the reciprocal cell has to be chosen with respect to the maximum gradient of diffuse scattering. Then the diffuse intensity may be described by a product of the real intensity distribution and the small reciprocal lattice. Fourier transformation yields the convolution of the real disordered structure and a large unit cell. In other words, the disordered structure is subdivided into large units and subsequently superimposed ('projected') in a single cell. In cases where a clear model of the disorder could be determined, a refinement procedure for atomic and other relevant parameters can be started. In this way a residual factor may be determined. A first approach has been elaborated by Epstein & Welberry (1983) in the case of substitutional disorder of two molecules.

The outstanding limiting factor is the collection of weak intensity data. The amount increases rapidly with the complexity of the structure and could even exceed by far the amount which is needed in the case of protein structure refinement. Hence, it seems to be reasonable to restrict the measurement to distinct areas in reciprocal space. Most of these publications, however, use too little information when compared with the minimum of data which would be necessary for the confirmation of the proposed model. Hence, physical and chemical considerations should be used as an additional source of information.

4.2.4.4.9. *Comparison between X-ray and neutron methods*

Apart from experimental arguments in favour of either method, there are some specific points which should be mentioned in this context. The diffuse scattering in question must be separated from Bragg scattering and from other diffuse-scattering contributions. Generally both methods are complementary: neutrons are preferable in cases where X-rays show only a small scattering contrast: (heavy) metal hydrides, oxides, carbides, Al–Mg distribution *etc.* In favourable cases it is possible to suppress (nuclear) Bragg scattering of neutrons when isotopes are used so that $\sum_\nu c_\nu f_\nu = 0$ for all equivalent positions. Another way to separate Bragg peaks is to record the diffuse intensity, if possible, at low $|\mathbf{H}|$ values. This can be achieved either by measurement at low θ angles or by using long wavelengths. For reasons of absorption the latter point is the domain of neutron scattering. Exceeding the Bragg cut-off, Bragg scattering is ruled out. In this way 'diffuse' background owing to multiple Bragg scattering is avoided. Other diffuse-scattering contributions which increase with the $|\mathbf{H}|$ value are thus also minimized: thermal diffuse scattering (TDS) and scattering due to long-range static displacements. On the other hand, lattice distortions, Huang scattering, . . . should be measured at large values of $|\mathbf{H}|$. TDS

can be separated by purely elastic neutron methods within the limits given by the energy resolution of an instrument. This technique is of particular importance at higher temperatures where TDS becomes remarkably strong. Neutron scattering is a good tool only in cases where (isotope/spin-)incoherent scattering is not too strong. In the case of magnetic materials confusion with paramagnetic diffuse scattering could occur. This is also important when electrons are trapped by defects which themselves act as paramagnetic centres.

As mentioned in Section 4.2.4.4.4 the evaluations of the γ, δ, ε depend on the assumption that the f's do not depend on $|\mathbf{H}|$ strongly within the range of measurement. Owing to the atomic form factor, this is not always well approximated in the X-ray case and is one of the main sources of error in the determination of the short-range-order parameters.

4.2.4.4.10. *Dynamic properties of defects*

Some brief remarks concerning the dynamic properties of defects as discussed in the previous sections now follow. Mass defects (impurity atoms), force-constant defects *etc.* influence the dynamic properties of the undistorted lattice and one could think of a modified TDS as discussed in Chapter 4.1. In the case of low defect concentrations special vibrational modes characterized by large amplitudes at the defect with frequency shifts and reduced lifetimes (resonant modes) or vibrational modes localized in space may occur. Other modes with frequencies near these particular modes may also be affected. Owing to the very low intensity of these phenomena their influence on the normal TDS is negligible and may be neglected in diffuse-scattering work. Theoretical treatments of crystals with higher defect concentrations are extremely difficult and not developed so far. For further reading see Böttger (1983).

4.2.4.5. *Orientational disorder*

Molecular crystals show in principle disorder phenomena similar to those discussed in previous sections (substitutional or displacement disorder). Here we have to replace the structure factors $F_\nu(\mathbf{H})$, used in the previous sections, by the molecular structure factors in their various orientations. Usually these are rapidly varying functions in reciprocal space which may obscure the disorder diffuse scattering. Disorder in molecular crystals is treated by Guinier (1963), Amorós & Amorós (1968), Flack (1970), Epstein *et al.* (1982), Welberry & Siripitayananon (1986, 1987), and others.

A particular type of disorder is very common in molecular and also in ionic crystals: the centres of masses of molecules or ionic complexes form a perfect 3D lattice but their orientations are disordered. Sometimes these solids are called plastic crystals. For comparison, the liquid-crystalline state is characterized by an orientational order in the absence of long-range positional order of the centres of the molecules. A clear-cut separation is not possible in cases where translational symmetry occurs in low dimension, *e.g.* in sheets or parallel to a few directions in crystal space. For discussion of these mesophases see Chapter 4.4.

An orientationally disordered crystal may be imagined in a static picture by freezing molecules in different sites in one of several orientations. Local correlations between neighbouring molecules and correlations between position and orientation may be responsible for orientational short-range order. Often thermal reorientations of the molecules are related to an orientationally disordered crystal. Thermal vibrations of the centres of masses of the molecules, librational or rotational excitations around one or more axes of the molecules, jumps between different equilibrium positions or diffusion-like phenomena are responsible for diffuse scattering of dynamic origin. As mentioned above the complexity of molecular structures and the associated large number of thermal modes complicate a separation from static disorder effects.

Generally high Debye–Waller factors are typical for scattering of orientationally disordered crystals. Consequently only a few Bragg reflections are observable. A large amount of structural information is stored in the diffuse background. It has to be analysed with respect to an incoherent and coherent part, elastic, quasielastic or inelastic nature, short-range correlations within one and the same molecule and between orientations of different molecules, and cross correlations between positional and orientational disorder scattering. Combined X-ray and neutron methods are therefore highly recommended.

4.2.4.5.1. *General expressions*

On the assumption of a well ordered 3D lattice, a general expression for the scattering by an orientationally disordered crystal with one molecule per unit cell may be given. This is a very common situation. Moreover, orientational disorder is frequently related to molecules with an overall 'globular' shape and consequently to crystals of high (in particular, averaged) spherical symmetry. In the following the relevant equations are given for this situation; these are discussed in some detail in a review article by Fouret (1979). The orientation of a molecule is characterized by a parameter ω_l, *e.g.* the set of Eulerian angles of three molecular axes with respect to the crystal axes: $\omega_l = 1, \ldots, D$ (D possible different orientations). The equilibrium position of the centre of mass of a molecule in orientation ω_l is given by $\mathbf{r}_l$, the equilibrium position of atom k within a molecule l in orientation ω_l by $\mathbf{r}_{lk}$ and a displacement from this equilibrium position by $\mathbf{u}_{lk}$. Averaging over a long time, *i.e.* supposing that the lifetime of a discrete configuration is long compared with the period of atomic vibrations, the observed intensity may be deduced from the intensity expression corresponding to a given configuration at time t:

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} F_l(\mathbf{H}, t) F_{l'}^+(\mathbf{H}, t)$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \qquad (4.2.4.85)$$

$$F_l(\mathbf{H}, t) = \sum_k f_k \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} + \mathbf{u}_{lk})\}. \qquad (4.2.4.86)$$

Averaging procedures must be carried out with respect to the thermal vibrations (denoted by an overbar) and over all configurations (symbol $\langle \ \rangle$). The centre-of-mass translational vibrations and librations of the molecules are most important in this context. (Internal vibrations of the molecules are assumed to be decoupled and remain unconsidered.)

$$I(\mathbf{H}, t) = \sum_l \sum_{l'} \langle \overline{F_l(\mathbf{H}, t) F_{l'}^+(\mathbf{H}, t)} \rangle$$
$$\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \qquad (4.2.4.85a)$$

Thermal averaging gives (*cf.* Chapter 4.1)

$$I = \sum_l \sum_{l'} \overline{F_l F_{l'}^+} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}$$

$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}$$
$$\times \overline{\exp\{2\pi i \mathbf{H} \cdot (\mathbf{u}_{lk} - \mathbf{u}_{l'k'})\}}. \qquad (4.2.4.87)$$

In the harmonic approximation $\overline{\exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{u}\}}$ is replaced by $\exp\{\frac{1}{2}|2\pi\mathbf{H} \cdot \Delta \mathbf{u}|^2\}$. This is, however, a more or less crude approximation because strongly anharmonic vibrations are quite common in an orientationally disordered crystal. In this approximation $\overline{F_l F_{l'}^+}$ becomes

$$\overline{F_l F_{l'}^+} = \sum_k \sum_{k'} f_k f_{k'} \exp\{-B_k(\omega_l)\}$$
$$\times \exp\{-B_{k'}(\omega_{l'})\} \exp\{D_{lk;\, l'k'}\}. \qquad (4.2.4.88)$$

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