

4. DIFFUSE SCATTERING AND RELATED TOPICS

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

Fourier transformation gives

$$I_d(\mathbf{H}) = N \left\{ \sum_{\nu} \alpha_{\nu} |F_{\nu}(\mathbf{H})|^2 - \sum_{\nu} \alpha_{\nu} F_{\nu}(\mathbf{H}) \sum_{\nu'} \alpha_{\nu'} F_{\nu'}^+(\mathbf{H}) \right\} \\ = N \{ \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \}. \quad (4.2.4.73)$$

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

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

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:

$$I_d(\mathbf{H}) = N \left\{ \sum_{\nu} \alpha_{\nu} [P'_{\nu\nu'}(\mathbf{H}) * L(\mathbf{H})] |F_{\nu}(\mathbf{H})|^2 \right. \\ + \sum_{\nu > \nu'} \alpha_{\nu} [\langle P'_{\nu\nu'}(\mathbf{H}) \rangle * L(\mathbf{H})] \\ \times [\Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) + \Delta F_{\nu}^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})] \\ + \sum_{\nu > \nu'} \alpha_{\nu} [\Delta P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \\ \left. \times [\Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}) - \Delta F_{\nu}^+(\mathbf{H}) \Delta F_{\nu'}(\mathbf{H})] \right\}. \quad (4.2.4.74)$$

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:

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

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: $f_{\nu}(\mathbf{r}) \exp\{2\pi i \mathbf{H} \cdot \Delta_{\nu\nu'} \mathbf{r}\}$. 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.*, \mathbf{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

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

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

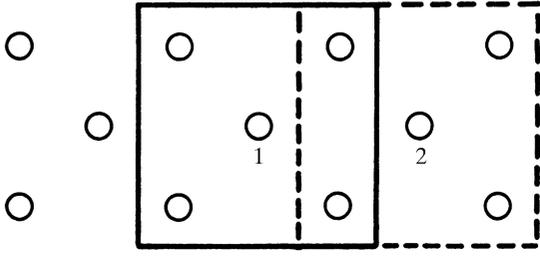


Fig. 4.2.4.1. Construction of the correlation function in the method of overlapping clusters.

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):

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

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:

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

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 (4.2.4.71b) 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:

$$\delta_{\mathbf{nn}'|AA} = \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|A} = x_{\mathbf{nn}'|AA}\mathbf{a} + y_{\mathbf{nn}'|AA}\mathbf{b} + z_{\mathbf{nn}'|AA}\mathbf{c}$$

$$\delta_{\mathbf{nn}'|AB} = \mathbf{u}_{\mathbf{n}|A} - \mathbf{u}_{\mathbf{n}'|B} = \dots$$

$$F_{\mathbf{nn}'|AA} = f_A^2 / (f_A - f_B)^2 \cdot [(c_A/c_B) + \alpha_{\mathbf{nn}'}]$$

$$F_{\mathbf{nn}'|BB} = f_B^2 / (f_A - f_B)^2 \cdot [(c_B/c_A) + \alpha_{\mathbf{nn}'}]$$

$$F_{\mathbf{nn}'|AB} = 2f_A f_B / (f_A - f_B)^2 \cdot (1 - \alpha_{\mathbf{nn}'}) = F_{\mathbf{nn}'|BA}$$