<center>4. DIFFUSE SCATTERING AND RELATED TOPICS</center>

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

Fourier transformation gives

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

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

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 $F_1 F_2 F_3$ 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:

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

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

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

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

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

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:

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

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

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

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