

4.2. Disorder diffuse scattering of X-rays and neutrons

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4.2.1. Scope of this chapter

Diffuse scattering of X-rays, neutrons and other particles is an accompanying effect in all diffraction experiments aimed at structure analysis with the aid of so-called elastic scattering. In this case the momentum exchange of the scattered photon (or particle) includes the crystal as a whole; the energy transfer involved becomes negligibly small and need not be considered in diffraction theory. Inelastic scattering processes, however, are due to excitation processes, such as ionization, phonon scattering *etc.* Distortions as a consequence of structural changes cause typical elastic or inelastic diffuse scattering. All these processes contribute to scattering, and a general theory has to include all of them. Hence, the exact treatment of diffuse scattering becomes very complex. Fortunately, approximations treating the phenomena independently are possible in most cases, but it should be kept in mind that difficulties may occasionally arise.

A separation of elastic from inelastic diffuse scattering may be made if detectors sensitive to the energy of radiation are used. Difficulties may sometimes result from small energy exchanges, which cannot be resolved for experimental reasons. The latter is true for scattering of X-rays by phonons which have energies of the order of 10^{-2} – 10^{-3} eV, a value which is considerably smaller than 10 keV, a typical value for X-ray quanta. Another equivalent explanation, frequently forwarded in the literature, is the high speed of X-ray photons, such that the rather slow motion of atoms cannot be ‘observed’ by them during diffraction. Hence, all movements appear as static displacement waves of atoms, and temperature diffuse scattering is pseudo-elastic for X-rays. This is not true in the case of thermal neutrons, which have energies comparable to those of phonons. Since thermal diffuse scattering is discussed in Chapter 4.1, this chapter is mainly concerned with the elastic (or pseudo-elastic other than thermal) part of diffuse scattering.

The full treatment of the complicated theoretical background for all other kinds of diffuse scattering lies beyond the scope of this article. It is also impossible to refer to all papers in this wide and complicated field. Different theoretical treatments of one and the same subject are often developed, but only some are given here, in most cases those which may be understood most easily – at least to the authors’ feeling. As shown in this chapter, electron-density fluctuations and distribution functions of defects play an important role for the complete interpretation of diffraction patterns. Both quantities may best be studied in the low-angle scattering range, which occasionally represents the only Bragg peak dealing with the full information of the distribution function of the defects. Hence, many problems cannot be solved without a detailed interpretation of low-angle diffraction.

Disorder phenomena in magnetic structures are not specifically discussed here. Magnetic diffuse neutron scattering and special experimental techniques themselves constitute a large subject. Many aspects, however, may be analysed along similar lines as given here. For this particular topic the reader is referred to textbooks of neutron scattering, where the theory of diffraction by magnetic materials is generally included (see, *e.g.*, Lovesey, 1984).

Glasses, liquids or liquid crystals show typical diffuse diffraction phenomena. Particle-size effects and strains have an important influence on the diffuse scattering. The same is true for dislocations and point defects such as interstitials or vacancies. These defects are mainly described by their strain field which influences the intensities of sharp reflections like an artificial temperature factor: the Bragg peaks diminish in intensity, while the diffuse scattering increases predominantly close to them. These phenomena are less important from a structural point of view, at least in the case of

metals or other simple structures. This statement is true as long as the structure of the ‘kernel’ of defects may be neglected when compared with the influence of the strain field. Whether dislocations in more complicated structures meet this condition is not yet known.

Radiation damage in crystals represents another field of diffuse scattering which cannot be treated here explicitly. As long as point defects only are generated, the strain field around these defects is the most important factor governing diffuse scattering. Particles with high energy, such as fast neutrons, protons and others, generate complicated defect structures which have to be treated with the aid of the cluster method described below, but no special reference is given here because of the complexity of these phenomena.

Diffuse scattering related to phase transitions, in particular the critical diffuse scattering observed at or close to the transition temperature, cannot be discussed here. In simple cases a satisfactory description may be given with the aid of a ‘soft phonon’, which freezes at the critical temperature, thus generating typical temperature-dependent diffuse scattering. If the geometry of the lattice is maintained during the transformation (no breakdown into crystallites of different cell geometry), the diffuse scattering is very similar to diffraction phenomena described in this article. Sometimes, however, very complicated interim stages (ordered or disordered) are observed demanding a complicated theory for their full explanation (see, *e.g.*, Dorner & Comes, 1977).

Commensurate and incommensurate modulated structures as well as quasicrystals are frequently accompanied by a typical diffuse scattering, demanding an extensive experimental and theoretical study in order to arrive at a satisfactory explanation. A reliable structure determination becomes very difficult in cases where the interpretation of diffuse scattering has not been incorporated. Many erroneous structural conclusions have been published in the past. The solution of problems of this kind needs careful thermodynamical consideration as to whether a plausible explanation of the structural data can be given.

Obviously, there is a close relationship between thermodynamics and diffuse scattering in disordered systems, representing a stable or metastable thermal equilibrium. From the thermodynamical point of view the system is then characterized by its grand partition function, which is intimately related to the correlation functions used in the interpretation of diffuse scattering. The latter is nothing other than a kind of ‘partial partition function’ where two atoms, or two cell occupations, are fixed such that the sum of all partial partition functions represents the grand partition function. This fact yields the useful correlation between thermodynamics and diffuse scattering mentioned above, which may well be used for a determination of thermodynamical properties of the crystal. This subject could not be included here for the following reason: real three-dimensional crystals generally exhibit diffuse scattering by defects and/or disordering effects which are not in thermal equilibrium. They are created during crystal growth, or are frozen-in defects formed at higher temperatures. Hence, a thermodynamical interpretation of diffraction data needs a careful study of diffuse scattering as a function of temperature or some other thermodynamical parameters. This can be done in very rare cases only, so the omission of this subject seems justified.

For all of the reasons mentioned above, this article cannot be complete. It is hoped, however, that it will provide a useful guide for those who need the information for the full understanding of the crystal chemistry of a given structure.

There is no comprehensive treatment of all aspects of diffuse scattering. Essential parts are treated in the textbooks of James (1954), Wilson (1962), Wooster (1962) and Schwartz & Cohen (1977); handbook articles are written by Jagodzinski (1963,

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1964a,b, 1987), Schulz (1982), Welberry (1985); and a series of interesting papers is collected by Collongues *et al.* (1977).

Many differences are caused by different symbols and by different 'languages' used in the various diffraction methods. Quite a few of the new symbols in use are not really necessary, but some are caused by differences in the experimental techniques. For example, the neutron scattering length b may usually be equated with the atomic form factor f in X-ray diffraction. The differential cross section introduced in neutron diffraction represents the intensity scattered into an angular range $d\Omega$ and an energy range dE . The famous scattering law in neutron work corresponds to the square of an (extended) structure factor; the 'static structure factor', a term used by neutron diffractionists, is nothing other than the conventional Patterson function. The complicated resolution functions in neutron work correspond to the well known Lorentz factors in X-ray diffraction. These have to be derived in order to include all techniques used in diffuse-scattering work.

4.2.2. Summary of basic scattering theory

Diffuse scattering results from deviations from the identity of translational invariant scattering objects and from long-range correlations in space and time. Fluctuations of scattering amplitudes and/or phase shifts of the scattered wavetrains reduce the maximum capacity of interference (leading to Bragg reflections) and are responsible for the diffuse scattering, *i.e.* scattering parts which are not located in reciprocal space in distinct spots. Unfortunately, the terms 'coherent' and 'incoherent' scattering used in this context are not uniquely defined in the literature. Since all scattering processes are correlated in space and time, there is no incoherent scattering at all in its strict sense. (A similar relationship exists for 'elastic' and 'inelastic' scattering. Here pure inelastic scattering would take place if the momentum and the energy were transferred to a single scatterer; on the other hand, an elastic scattering process would demand a uniform exchange of momentum and energy with the whole crystal.) Obviously, both cases are idealized and the truth lies somewhere in between. In spite of this, a great many authors use the term 'incoherent' systematically for the diffuse scattering away from the Bragg peaks, even if some diffuse maxima or minima, other than those due to structure factors of molecules or atoms, are observed. Although this definition is unequivocal as such, it is physically incorrect. Other authors use the term 'coherent' for Bragg scattering only; all diffuse contributions are then called 'incoherent'. This definition is clear and unique since it considers space and time, but it does not differentiate between incoherent and inelastic. In the case of neutron scattering both terms are essential and cannot be abandoned.

In neutron diffraction the term 'incoherent' scattering is generally used in cases where no correlation between spin orientations or between isotopes of the same element exists. Hence, another definition of 'incoherence' is proposed for scattering processes that are uncorrelated in space and time. In fact there may be correlations between the spins *via* their magnetic field, but the correlation length in space (and time) may be very small, such that the scattering process appears to be incoherent. Even in these cases the nuclei contribute to coherent (average structure) and incoherent scattering (diffuse background). Hence, the scattering process cannot really be understood by assuming nuclei which scatter independently. For this reason, it seems to be useful to restrict the term 'incoherent' to cases where a random contribution to scattering is realized or, in other words, a continuous function exists in reciprocal space. This corresponds to a δ function in real four-dimensional space. The randomness may be attributed to a nucleus (neutron diffraction) or an atom (molecule). It follows from this definition that the scattering need not be continuous, but

may be modulated by structure factors of molecules. In this sense we shall use the term 'incoherent', remembering that it is incorrect from a physical point of view.

As mentioned in Chapter 4.1 the theory of thermal neutron scattering must be treated quantum mechanically. (In principle this is true also in the X-ray case.) In the classical limit, however, the final expressions have a simple physical interpretation. Generally, the quantum-mechanical nature of the scattering function of thermal neutrons is negligible at higher temperatures and in those cases where energy or momentum transfers are not too large. In almost all disorder problems this classical interpretation is sufficient for interpretation of diffuse scattering phenomena. This is not quite true in the case of orientational disorder (plastic crystals) where H atoms are involved.

The basic formulae given below are valid in either the X-ray or the neutron case: the atomic form factor f replaces the coherent scattering length b_{coh} (abbreviated to b). The formulation in the frame of the van Hove correlation function $G(\mathbf{r}, t)$ (classical interpretation, coherent part) corresponds to a treatment by a four-dimensional Patterson function $P(\mathbf{r}, t)$.

The basic equations for the differential cross sections are:

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}| \langle b \rangle^2}{|\mathbf{k}_0| 2\pi\hbar} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}| \langle b^2 \rangle - \langle b \rangle^2}{|\mathbf{k}_0| 2\pi\hbar} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1b)$$

(N = number of scattering nuclei of same chemical species; \mathbf{k} , \mathbf{k}_0 = wavevectors after/before scattering).

The integrations over space may be replaced by summations in disordered crystals except for cases where structural elements exhibit a liquid-like behaviour. Then the van Hove correlation functions are:

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j, \mathbf{r}_j'} \delta\{\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \quad (4.2.2.2a)$$

$$G_s(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j} \delta\{\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\}. \quad (4.2.2.2b)$$

$G(\mathbf{r}, t)$ gives the probability that if there is an atom j at $\mathbf{r}_j(0)$ at time zero, there is an *arbitrary* atom j' at $\mathbf{r}_j'(t)$ at *arbitrary* time t , while $G_s(\mathbf{r}, t)$ refers to the *same* atom j at $\mathbf{r}_j(t)$ at time t .

Equations (4.2.2.1) may be rewritten by use of the four-dimensional Fourier transforms of G , and G_s , respectively:

$$S_{\text{coh}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3a)$$

$$S_{\text{inc}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3b)$$

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} \langle b \rangle^2 S_{\text{coh}}(\mathbf{H}, \omega) \quad (4.2.2.4a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} [\langle b^2 \rangle - \langle b \rangle^2] S_{\text{inc}}(\mathbf{H}, \omega). \quad (4.2.2.4b)$$

Incoherent scattering cross sections [(4.2.2.3b), (4.2.2.4b)] refer to one and the same particle (at different times). In particular, plastic crystals (see Section 4.2.4.5) may be studied by means of this

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incoherent scattering. It should be emphasized, however, that for reasons of intensity only disordered crystals with strong incoherent scatterers can be investigated by this technique. In practice, mostly samples with hydrogen atoms were investigated. This topic will not be treated further in this article (see, *e.g.*, Springer, 1972; Lechner & Riekkel, 1983). The following considerations are restricted to *coherent* scattering only.

Essentially the same formalism as given by equations (4.2.2.1a)–(4.2.2.4a) may be described by the use of a generalized Patterson function, which is more familiar to crystallographers,

$$P(\mathbf{r}, t) = \int_{\mathbf{r}'} \int_{t'=0}^{\tau} \rho(\mathbf{r}', t') \rho(\mathbf{r}' + \mathbf{r}, t' + t) d\mathbf{r}' dt', \quad (4.2.2.5)$$

where τ denotes the time of observation. The only difference between $G(\mathbf{r}, t)$ and $P(\mathbf{r}, t)$ is the inclusion of the scattering weight (f or b) in $P(\mathbf{r}, t)$. $P(\mathbf{r}, t)$ is an extension of the usual spatial Patterson function $P(\mathbf{r})$.

$$\begin{aligned} P(\mathbf{r}, t) &\leftrightarrow 2\pi S(\mathbf{H}, \omega) \equiv |F(\mathbf{H}, \omega)|^2 \\ &= \int_{\mathbf{r}} \int_t P(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt. \end{aligned} \quad (4.2.2.6)$$

One difficulty arises from neglecting the time of observation. Just as $S(\mathbf{H})$ ($\sim |F(\mathbf{H})|^2$) is always proportional to the scattering volume V , in the frame of a kinematical theory or within Born's first approximation [*cf.* equation (4.2.2.1a)], so $S(\mathbf{H}, \omega)$ [$\sim |F(\mathbf{H}, \omega)|^2$] is proportional to volume *and* observation time. Generally one does not make S proportional to V , but one normalizes S to be independent of τ as $\tau \rightarrow \infty$: $2\pi S = (1/\tau)|F|^2$. Averaging over time τ gives therefore

$$\begin{aligned} S(\mathbf{H}, \omega) &= \frac{1}{2\pi} \int_{\mathbf{r}} \int_t \left\langle \int_{\mathbf{r}'} \rho(\mathbf{r}', t') \rho(\mathbf{r}' + \mathbf{r}, t' + t) d\mathbf{r}' \right\rangle_t \\ &\quad \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt. \end{aligned} \quad (4.2.2.7)$$

Special cases (see, *e.g.*, Cowley, 1981):

(1) *Pure elastic measurement*

$$\begin{aligned} I_e \sim S(\mathbf{H}, 0) &= \int_{\mathbf{r}} \left[\int_t P(\mathbf{r}, t) dt \right] \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \\ &= \left| \sum_j f_j \langle \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}_j(t)\} \rangle_t \right|^2. \end{aligned} \quad (4.2.2.8)$$

In this type of measurement the time-averaged 'structure' is determined:

$$\langle \rho(\mathbf{r}, t) \rangle_t = \int_{\mathbf{H}} |F(\mathbf{H}, 0)| \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{H}.$$

The projection along the time axis in real (Patterson) space gives a section in Fourier space at $\omega = 0$. True elastic measurement is a domain of neutron scattering. For a determination of the time-averaged structure of a statistically disordered crystal dynamical disorder (phonon scattering) may be separated. For liquids or liquid-like systems this kind of scattering technique is rather ineffective as the time-averaging procedure gives a uniform particle distribution only.

(2) *Integration over frequency (or energy)*

$$\begin{aligned} I_{\text{tot}} &\sim \int_{\omega} |F(\mathbf{H}, \omega)|^2 d\omega = \int_{\omega} \int_{\mathbf{r}} \int_t P(\mathbf{r}, t) \\ &\quad \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt d\omega \\ &= \int_{\mathbf{r}} P(\mathbf{r}, 0) \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \end{aligned} \quad (4.2.2.9)$$

(*cf.* properties of δ functions). In such an experiment one determines

the Patterson function for $t = 0$, *i.e.* the instantaneous structure ('snapshot' of the correlation function): a projection in Fourier space along the energy axis gives a section in direct (Patterson) space at $t = 0$. An energy integration is automatically performed in a conventional X-ray diffraction experiment ($|\mathbf{k}| \sim |\mathbf{k}_0|$). One should keep in mind that in a real experiment there is, of course, an average over both the sample volume and the time of observation.

In most practical cases averaging over time is equivalent to averaging over space: the total diffracted intensity may be regarded as the sum of intensities from a large number of independent regions due to the limited coherence of a beam. At any time these regions take all possible configurations. Therefore, this sum of intensities is equivalent to the sum of intensities from any one region at different times:

$$\begin{aligned} \langle I_{\text{tot}} \rangle_t &= \left\langle \sum_j \sum_{j'} f_j f_{j'} \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})\} \right\rangle_t \\ &= \sum_{j, j'} f_j f_{j'} \langle \exp\{2\pi i\mathbf{H} \cdot (\mathbf{r}_j - \mathbf{r}_{j'})\} \rangle_t. \end{aligned} \quad (4.2.2.9a)$$

From the basic formulae one also derives the well known results of X-ray or neutron scattering by a periodic arrangement of particles in space [*cf.* equation (4.1.3.2) of Chapter 4.1]:

$$\frac{d\sigma}{d\Omega} = N \frac{(2\pi)^3}{V_c} \sum_{\mathbf{h}} |F(\mathbf{H})|^2 \delta(\mathbf{H} - \mathbf{h}) \quad (4.2.2.10)$$

$$F(\mathbf{H}) = \sum_j f_j(\mathbf{H}) \exp\{-W_j\} \exp\{2\pi i\mathbf{H} \cdot \mathbf{r}_j\}. \quad (4.2.2.11)$$

$F(\mathbf{H})$ denotes the Fourier transform of one cell (structure factor); the f_j 's are assumed to be real.

The evaluation of the intensity expressions (4.2.2.6), (4.2.2.8) or (4.2.2.9), (4.2.2.9a) for a disordered crystal must be performed in terms of statistical relationships between scattering factors and/or atomic positions.

From these basic concepts the generally adopted method in a disorder problem is to try to separate the scattering intensity into two parts, namely one part $\langle \rho \rangle$ from an average periodic structure where formulae (4.2.2.10), (4.2.2.11) apply and a second part $\Delta\rho$ resulting from fluctuations from this average (see, *e.g.*, Schwartz & Cohen, 1977). One may write formally:

$$\rho = \langle \rho \rangle + \Delta\rho, \quad (4.2.2.12a)$$

where $\langle \rho \rangle$ is defined to be time independent and periodic in space and $\langle \Delta\rho \rangle = 0$. Because cross terms $\langle \rho \rangle * \Delta\rho$ vanish by definition, the Patterson function is

$$\begin{aligned} &[\langle \rho(\mathbf{r}) \rangle + \Delta\rho(\mathbf{r})] * [\langle \rho(-\mathbf{r}) \rangle + \Delta\rho(-\mathbf{r})] \\ &= [\langle \rho(\mathbf{r}) \rangle * \langle \rho(-\mathbf{r}) \rangle] + [\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})]. \end{aligned} \quad (4.2.2.12b)$$

Fourier transformation gives

$$I \approx |\langle F \rangle|^2 + |\Delta F|^2 \quad (4.2.2.13a)$$

$$|\Delta F|^2 = \langle |F|^2 \rangle - |\langle F \rangle|^2. \quad (4.2.2.13b)$$

Since $\langle \rho \rangle$ is periodic, the first term in (4.2.2.13) describes Bragg scattering where $\langle F \rangle$ plays the normal role of a structure factor of one cell of the averaged structure. The second term corresponds to diffuse scattering. In many cases diffuse interferences are centred exactly at the positions of the Bragg reflections. It is then a serious experimental problem to decide whether the observed intensity distribution is Bragg scattering obscured by crystal-size limitations or other scattering phenomena.

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If disordering is time dependent exclusively, $\langle \rho \rangle$ represents the time average, whereas $\langle F \rangle$ gives the pure elastic scattering part [cf. equation (4.2.2.8)] and ΔF refers to inelastic scattering only.

4.2.3. General treatment

4.2.3.1. Qualitative interpretation of diffuse scattering

Any structure analysis of disordered structures should start with a qualitative interpretation of diffuse scattering. This problem may be facilitated with the aid of Fourier transforms and their algebraic operations (see, e.g., Patterson, 1959). For simplicity the following modified notation is used in this section: functions in real space are represented by small letters, e.g. $a(\mathbf{r})$, $b(\mathbf{r})$, . . . except for $F(\mathbf{r})$ and $P(\mathbf{r})$ which are used as general symbols for a structure and the Patterson function, respectively; functions in reciprocal space are given by capital letters $A(\mathbf{H})$, $B(\mathbf{H})$; \mathbf{r} and \mathbf{H} are general vectors in real and reciprocal space, respectively, $H_x + Ky + Lz$ is the scalar product $\mathbf{H} \cdot \mathbf{r}$; $d\mathbf{r}$ and $d\mathbf{H}$ indicate integrations in three dimensions in real and reciprocal space, respectively. Even for X-rays the electron density $\rho(\mathbf{r})$ will generally be replaced by the scattering potential $a(\mathbf{r})$. Consequently, anomalous contributions to scattering may be included if complex functions $a(\mathbf{r})$ are admitted. In the neutron case $a(\mathbf{r})$ refers to a quasi-potential. Using this notation we obtain the scattered amplitude and phase $A(\mathbf{H}) \exp i\varphi$

$$A(\mathbf{H}) = \int_{\mathbf{r}} a(\mathbf{r}) \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{r} \quad (4.2.3.1a)$$

$$a(\mathbf{r}) = \int_{\mathbf{H}} A(\mathbf{H}) \exp\{-2\pi i \mathbf{H} \cdot \mathbf{r}\} d\mathbf{H} \quad (4.2.3.1b)$$

(constant factors are omitted).

$a(\mathbf{r})$ and $A(\mathbf{H})$ are reversibly and uniquely determined by Fourier transformation. Consequently equations (4.2.3.1) may simply be replaced by $a(\mathbf{r}) \leftrightarrow A(\mathbf{H})$, where the double-headed arrow represents the two integrations given by (4.2.3.1) and means: $A(\mathbf{H})$ is the Fourier transform of $a(\mathbf{r})$, and *vice versa*. The following relations may easily be derived from (4.2.3.1):

$$a(\mathbf{r}) + b(\mathbf{r}) \leftrightarrow A(\mathbf{H}) + B(\mathbf{H}) \quad (\text{law of addition}) \quad (4.2.3.2)$$

$$\beta a(\mathbf{r}) \leftrightarrow \beta A(\mathbf{H}) \quad (\text{law of scalar multiplication}) \quad (4.2.3.3)$$

(β = scalar quantity).

On the other hand, the multiplication of two functions does not yield a relation of similar symmetrical simplicity:

$$\begin{aligned} a(\mathbf{r})b(\mathbf{r}) &\leftrightarrow \int A(\mathbf{H}')B(\mathbf{H} - \mathbf{H}') d\mathbf{H}' \\ &= A(\mathbf{H}) * B(\mathbf{H}) \end{aligned} \quad (4.2.3.4a)$$

$$\begin{aligned} a(\mathbf{r}) * b(\mathbf{r}) &= \int a(\mathbf{r}')b(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\ &\leftrightarrow A(\mathbf{H})B(\mathbf{H}) \end{aligned} \quad (4.2.3.4b)$$

(laws of convolution and multiplication).

Since $a(\mathbf{r})b(\mathbf{r}) = b(\mathbf{r})a(\mathbf{r})$:

$$\int A(\mathbf{H}')B(\mathbf{H} - \mathbf{H}') d\mathbf{H}' = \int B(\mathbf{H}')A(\mathbf{H} - \mathbf{H}') d\mathbf{H}'$$

and *vice versa*. The convolution operation is commutative in either space.

For simplicity the symbol $a(\mathbf{r}) * b(\mathbf{r})$ instead of the complete convolution integral is used. The distribution law $a(b + c) = ab + ac$ is valid for the convolution as well:

$$a(\mathbf{r}) * [b(\mathbf{r}) + c(\mathbf{r})] = a(\mathbf{r}) * b(\mathbf{r}) + a(\mathbf{r}) * c(\mathbf{r}). \quad (4.2.3.5)$$

The associative law of multiplication does not hold if mixed products (convolution and multiplication) are used:

$$a(\mathbf{r}) * [b(\mathbf{r})c(\mathbf{r})] \neq [a(\mathbf{r}) * b(\mathbf{r})]c(\mathbf{r}). \quad (4.2.3.6)$$

From equations (4.2.3.1) one has:

$$\begin{aligned} a(\mathbf{r} - \mathbf{r}_0) &\leftrightarrow A(\mathbf{H}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_0) \\ A(\mathbf{H} - \mathbf{H}_0) &\leftrightarrow a(\mathbf{r}) \exp(-2\pi i \mathbf{H}_0 \cdot \mathbf{r}) \end{aligned} \quad (4.2.3.7)$$

(law of displacements).

Since symmetry operations are well known to crystallographers in reciprocal space also, the law of inversion is mentioned here only:

$$a(-\mathbf{r}) \leftrightarrow A(-\mathbf{H}). \quad (4.2.3.8)$$

Consequently, if $a(\mathbf{r}) = a(-\mathbf{r})$, then $A(\mathbf{H}) = A(-\mathbf{H})$. In order to calculate the intensity the complex conjugate $A^+(\mathbf{H})$ is needed:

$$a^+(\mathbf{r}) \leftrightarrow A^+(-\mathbf{H}) \quad (4.2.3.9a)$$

$$a^+(-\mathbf{r}) \leftrightarrow A^+(\mathbf{H}). \quad (4.2.3.9b)$$

Equations (4.2.3.9) yield the relationship $A^+(-\mathbf{H}) = A(\mathbf{H})$ ('Friedel's law') if $a(\mathbf{r})$ is a *real* function. The multiplication of a function with its conjugate is given by:

$$a(\mathbf{r}) * a^+(-\mathbf{r}) \leftrightarrow |A(\mathbf{H})|^2,$$

with

$$a(\mathbf{r}) * a^+(-\mathbf{r}) = \int a(\mathbf{r}')a(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P(\mathbf{r}). \quad (4.2.3.10)$$

Note that $P(\mathbf{r}) = P(-\mathbf{r})$ is not valid if $a(\mathbf{r})$ is complex. Consequently $|A(-\mathbf{H})|^2 \neq |A(\mathbf{H})|^2$. This is shown by evaluating $A(-\mathbf{H})A^+(-\mathbf{H})$

$$A(-\mathbf{H})A^+(-\mathbf{H}) \leftrightarrow a(-\mathbf{r}) * a^+(\mathbf{r}) = P(-\mathbf{r}). \quad (4.2.3.11)$$

Equation (4.2.3.11) is very useful for the determination of the contribution of anomalous scattering to diffuse reflections.

Most of the diffuse diffraction phenomena observed may be interpreted qualitatively or even semi-quantitatively in a very simple manner using a limited number of important Fourier transforms, given below.

4.2.3.1.1. Fourier transforms

(1) Normalized Gaussian function

$$(\pi^{3/2} \alpha \beta \gamma)^{-1} \exp\{-(x/\alpha)^2 - (y/\beta)^2 - (z/\gamma)^2\}. \quad (4.2.3.12)$$

This plays an important role in statistics. Its Fourier transform is again a Gaussian:

$$\exp\{-\pi^2(\alpha^2 H^2 + \beta^2 K^2 + \gamma^2 L^2)\}. \quad (4.2.3.12a)$$

The three parameters α , β , γ determine the width of the curve. Small values of α , β , γ represent a broad maximum in reciprocal space but a narrow one in real space, and *vice versa*. The constant has been chosen such that the integral of the Gaussian is unity in real space. The product of two Gaussians in reciprocal space

$$\begin{aligned} &\exp\{-\pi^2(\alpha_1^2 H^2 + \beta_1^2 K^2 + \gamma_1^2 L^2)\} \\ &\times \exp\{-\pi^2(\alpha_2^2 H^2 + \beta_2^2 K^2 + \gamma_2^2 L^2)\} \\ &= \exp\{-\pi^2[(\alpha_1^2 + \alpha_2^2)H^2 + (\beta_1^2 + \beta_2^2)K^2 \\ &\quad + (\gamma_1^2 + \gamma_2^2)L^2]\} \end{aligned} \quad (4.2.3.12b)$$

again represents a Gaussian of the same type, but with a sharper profile. Consequently its Fourier transform given by the convolution of the transforms of the two Gaussians is itself a Gaussian with a broader maximum. It may be concluded from this discussion that the Gaussian with $\alpha, \beta, \gamma \rightarrow 0$ is a δ function in real space, and its Fourier transform is unity in reciprocal space. The convolution of two δ functions is again a δ function.

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(2) Lattices

Lattices in real and reciprocal space may be described by δ functions

$$l(\mathbf{r}) = \sum_{\mathbf{n}} \delta(\mathbf{r} - \mathbf{n})$$

and

$$L(\mathbf{H}) = \sum_{\mathbf{h}} \delta(\mathbf{H} - \mathbf{h}),$$

where \mathbf{n} , \mathbf{h} represent the components of the displacement vectors in real and reciprocal space, respectively. The Fourier transforms of lattices with orthogonal basis vectors of unit length and an infinite number of points in all three dimensions correspond to each other. In the following the relation $l(\mathbf{r}) \leftrightarrow L(\mathbf{H})$ is used in this generalized sense.

The Fourier transforms of *finite* lattices are given by

$$\frac{\sin \pi N_1 H}{\sin \pi H} \frac{\sin \pi N_2 K}{\sin \pi K} \frac{\sin \pi N_3 L}{\sin \pi L}, \quad (4.2.3.13)$$

which is a periodic function in reciprocal space, but, strictly speaking, non-periodic in real space. It should be pointed out that the correspondence of lattices in either space is valid only if the origin coincides with a δ function. This fact may easily be understood by applying the law of displacement given in equation (4.2.3.7).

(3) Box functions

The Fourier transform of a box function $b(\mathbf{r})$ with unit height is:

$$b(\mathbf{r}) \leftrightarrow \frac{\sin \pi \alpha H}{\pi H} \frac{\sin \pi \beta K}{\pi K} \frac{\sin \pi \gamma L}{\pi L}. \quad (4.2.3.14)$$

α , β , γ describe its extension in the three dimensions. This function is real as long as the centre of symmetry is placed at the origin, otherwise the law of displacement has to be used. The convolution of the box function is needed for the calculation of intensities:

$$t(\mathbf{r}) = b(\mathbf{r}) * b(-\mathbf{r}) \\ \leftrightarrow \left(\frac{\sin \pi \alpha H}{\pi H} \right)^2 \left(\frac{\sin \pi \beta K}{\pi K} \right)^2 \left(\frac{\sin \pi \gamma L}{\pi L} \right)^2. \quad (4.2.3.15)$$

$t(\mathbf{r})$ is a generalized three-dimensional ‘pyramid’ of doubled basal length when compared with the corresponding length of the box function. The top of the pyramid has a height given by the number of unit cells covered by the box function. Obviously, the box function generates a particle size in real space by multiplying the infinite lattice $l(\mathbf{r})$ by $b(\mathbf{r})$. Fourier transformation yields a particle-size effect well known in diffraction. Correspondingly, the termination effect of a Fourier synthesis is caused by multiplication by a box function in reciprocal space, which causes a broadening of maxima in real space.

(4) Convolutions

It is often very useful to elucidate the convolution given in equations (4.2.3.4) by introducing the corresponding pictures in real or reciprocal space. Since $1 \cdot f(\mathbf{r}) = f(\mathbf{r})$, $\delta(\mathbf{H}) * F(\mathbf{H}) = F(\mathbf{H})$ the convolution with a δ function must result in an identical picture of the second function, although the function is used as $f(-\mathbf{r})$ in the integrals of equations (4.2.3.4), $f(\mathbf{r} - \mathbf{r}')$ with \mathbf{r}' as variable in the integral of convolution. The convolution with $f(-\mathbf{r})$ brings the integral into the form

$$\int f(\mathbf{r}') f(\mathbf{r}' - \mathbf{r}) d\mathbf{r}', \quad (4.2.3.16)$$

which is known as the Patterson function (or self- or auto-

convolution) and represents the generalized Patterson function including anomalous scattering [cf. equation (4.2.3.10)].

The change of the variable in the convolution integral may sometimes lead to confusion if certain operations are applied to the arguments of the functions entering the integral. Hence, it seems to be useful to mention the invariance of the convolution integral with respect to a change of sign, or a displacement, respectively, if applied to \mathbf{r}' in both functions. Consequently, the convolution with the inverted function $a(\mathbf{r}) * b(-\mathbf{r})$ may be determined as follows:

$$b'(\mathbf{r}) = b(-\mathbf{r}) \\ a(\mathbf{r}) * b(-\mathbf{r}) = a(\mathbf{r}) * b'(\mathbf{r}) = \int a(\mathbf{r}') b'(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\ = \int a(\mathbf{r}') b(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = P'(\mathbf{r}). \quad (4.2.3.17)$$

This equation means that the second function is displaced into the positive direction by \mathbf{r} , then multiplied by the first function and integrated. In the original meaning of the convolution the operation represents a displacement of the second function into the positive direction and an inversion at the displaced origin before multiplication and subsequent integration. On comparing both operations it may be concluded that $P'(\mathbf{r}) \neq P'(-\mathbf{r})$ if the second function is acentric. For real functions both have to be acentric. In a similar way it may be shown that the convolution of

$$a(\mathbf{r} - \mathbf{m}) * b(\mathbf{r} - \mathbf{m}') = \int_{\mathbf{r}'} a(\mathbf{r}' - \mathbf{m}) b(\mathbf{r} - \mathbf{m}' - \mathbf{r}') d\mathbf{r}' \\ = \int_{\mathbf{r}''} a(\mathbf{r}'') b(\mathbf{r} - \mathbf{m}' - \mathbf{m} - \mathbf{r}'') d\mathbf{r}'' \quad (4.2.3.18)$$

Equation (4.2.3.18) indicates a displacement by $\mathbf{m}' + \mathbf{m}$ with respect to the convolution of the undisplaced functions. Consequently

$$\delta(\mathbf{r} - \mathbf{m}) * \delta(\mathbf{r} - \mathbf{m}') = \delta(\mathbf{r} - \mathbf{m} - \mathbf{m}'). \quad (4.2.3.19)$$

Obviously, the commutative law of convolution is obeyed; on the other hand, the convolution with the inverted function yields

$$\delta(\mathbf{r} - \mathbf{m}' + \mathbf{m}),$$

indicating that the commutative law (interchange of \mathbf{m} and \mathbf{m}') is violated because of the different signs of \mathbf{m} and \mathbf{m}' .

The effectiveness of the method outlined above may be greatly improved by introducing further Fourier transforms of useful functions in real and reciprocal space (Patterson, 1959).

4.2.3.1.2. Applications

(1) Clusters in a periodic lattice (low concentrations)

The exsolution of clusters of equal sizes is considered. The lattice of the host is undistorted and the clusters have the same lattice but a different structure. A schematic drawing is shown in Fig. 4.2.3.1. Two different structures are introduced by

$$F_1(\mathbf{r}) = \sum_{\nu} \delta(\mathbf{r} - \mathbf{r}_{\nu}) * F_{\nu}(\mathbf{r}) \\ F_2(\mathbf{r}) = \sum_{\mu} \delta(\mathbf{r} - \mathbf{r}_{\mu}) * F_{\mu}(\mathbf{r}).$$

Their Fourier transforms are the structure factors $F_1(\mathbf{H})$, $F_2(\mathbf{H})$. The bold lines in Fig. 4.2.3.1 indicate the clusters, which may be represented by box functions $b(\mathbf{r})$ in the simplest case. It should be pointed out, however, that a more complicated shape means nothing other than a replacement of $b(\mathbf{r})$ by another shape function $b'(\mathbf{r})$ and its Fourier transform $B'(\mathbf{H})$. The distribution of clusters is represented by

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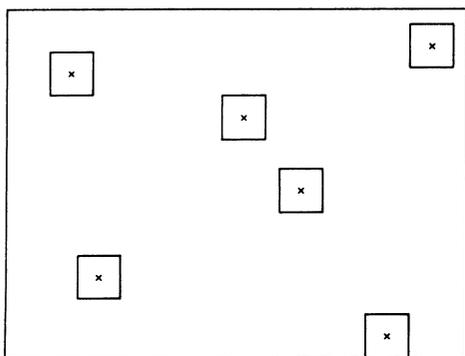


Fig. 4.2.3.1. Model of the two-dimensional distribution of point defects, causing changes in the surroundings.

$$d(\mathbf{r}) = \sum_{\mathbf{m}} \delta(\mathbf{r} - \mathbf{m}),$$

where \mathbf{m} refers to the centres (crosses in Fig. 4.2.3.1) of the box functions. The problem is therefore defined by:

$$l(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b(\mathbf{r})] * [F_2(\mathbf{r}) - F_1(\mathbf{r})] * d(\mathbf{r}). \quad (4.2.3.20a)$$

The incorrect addition of $F_1(\mathbf{r})$ to the areas of clusters $F_2(\mathbf{r})$ is compensated by subtracting the same contribution from the second term in equation (4.2.3.20a). In order to determine the diffuse scattering the Fourier transformation of (4.2.3.20a) is performed:

$$L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}). \quad (4.2.3.20b)$$

The intensity is given by

$$|L(\mathbf{H})F_1(\mathbf{H}) + [L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2. \quad (4.2.3.20c)$$

Evaluation of equation (4.2.3.20c) yields three terms (c.c. means complex conjugate):

- (i) $|L(\mathbf{H})F_1(\mathbf{H})|^2$
- (ii) $\{[L(\mathbf{H})F_1(\mathbf{H})][L(\mathbf{H}) * B(\mathbf{H})] \times [F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H}) + \text{c.c.}\}$
- (iii) $|[L(\mathbf{H}) * B(\mathbf{H})][F_2(\mathbf{H}) - F_1(\mathbf{H})]D(\mathbf{H})|^2$.

The first two terms represent modulated lattices [multiplication of $L(\mathbf{H})$ by $F_1(\mathbf{H})$]. Consequently, they cannot contribute to diffuse scattering which is completely determined by the third term. Fourier transformation of this term gives $[l(\mathbf{r}) = l(-\mathbf{r}); b(\mathbf{r}) = b(-\mathbf{r}); \Delta F = F_2 - F_1]$:

$$\begin{aligned} & [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * d(\mathbf{r}) * [l(\mathbf{r})b(\mathbf{r})] * \Delta F^+(-\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})b(\mathbf{r})] * [l(\mathbf{r})b(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}) \\ &= [l(\mathbf{r})t(\mathbf{r})] * \Delta F(\mathbf{r}) * \Delta F^+(-\mathbf{r}) * d(\mathbf{r}) * d(-\mathbf{r}). \quad (4.2.3.21a) \end{aligned}$$

According to equation (4.2.3.15) and its subsequent discussion the convolution of the two expressions in square brackets was replaced by $l(\mathbf{r})t(\mathbf{r})$, where $t(\mathbf{r})$ represents the 'pyramid' of n -fold height discussed above and n is the number of unit cells within $b(\mathbf{r})$. $d(\mathbf{r}) * d(-\mathbf{r})$ is the Patterson function of the distribution function $d(\mathbf{r})$. Its usefulness may be recognized by considering the two possible extreme solutions, namely the random and the strictly periodic distribution.

If no fluctuations of domain sizes are admitted the minimum distance between two neighbouring domains is equal to the length of the domain in the corresponding direction. This means that the distribution function cannot be completely random. In one

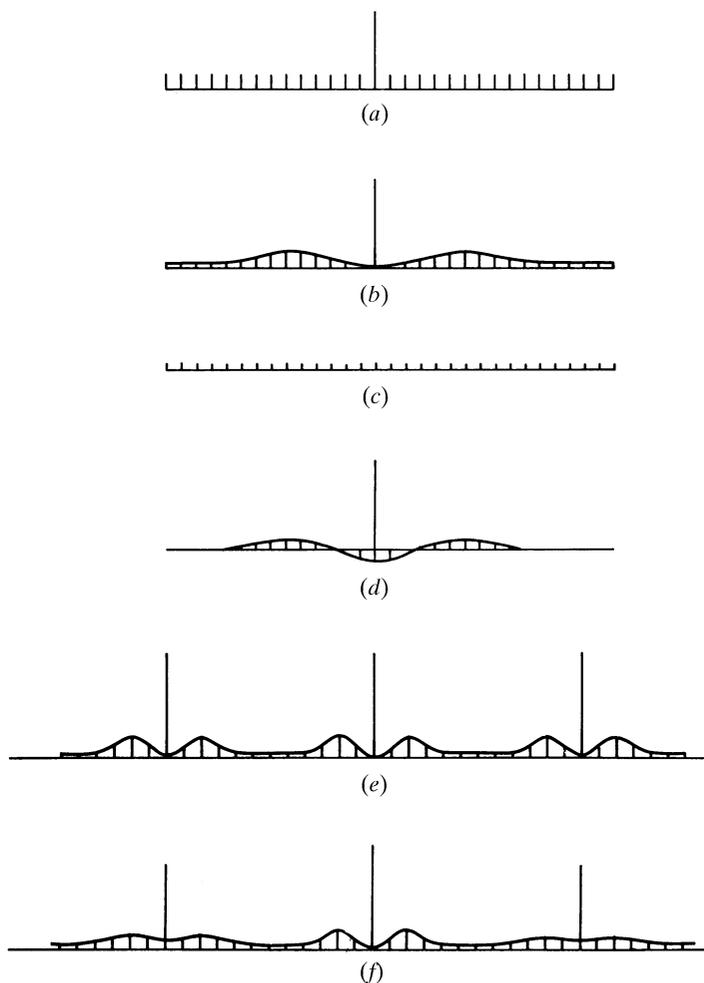


Fig. 4.2.3.2. One-dimensional Patterson functions of various point-defect distributions: (a) random distribution; (b) influence of finite volume of defects on the distribution function; (c), (d) decomposition of (b) into a periodic (c) and a convergent (d) part; (e) Fourier transform of (c) + (d); (f) changes of (e), if the centres of the defects show major deviations from the origins of the lattice.

dimension the solution of a random distribution of particles of a given size on a finite length shows that the distribution functions exhibit periodicities depending on the average free volume of one particle (Zernike & Prins, 1927). Although the problem is more complicated in three dimensions, there should be no fundamental difference in the exact solutions.

On the other hand, it may be shown that the convolution of a pseudo-random distribution may be obtained if the average free volume is large. This is shown in Fig. 4.2.3.2(a) for the particular case of a cluster smaller than one unit cell. A strictly periodic distribution function (superstructure) may result, however, if the volume of the domain and the average free volume are equal. Obviously, the practical solution for the self-convolution of the distribution function (= Patterson function) lies somewhere in between, as shown in Fig. 4.2.3.2(b). If a harmonic periodicity damped by a Gaussian is assumed, this self-convolution of the distribution in real space may be considered to consist of two parts, as shown in Figs. 4.2.3.2(c), (d). Note that the two different solutions result in completely different diffraction patterns:

(i) The geometrically perfect lattice extends to distances which are large when compared with the correlation length of the distribution function. Then the Patterson function of the distribution function concentrates at the positions of the basic lattice, which is

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given by multiplication by the lattice $l(\mathbf{r})$. The corresponding convolution in reciprocal space gives the same contribution to all Bragg reflections (Fig. 4.2.3.2e).

(ii) There is no perfect lattice geometry. In this case a continuous Patterson function results. Fourier transformation yields an influence which is now restricted primarily to the reflection 000, *i.e.* to the low-angle diffraction range.

Figs. 4.2.3.2(e), (f) show the different diffraction patterns of the diffuse scattering which is concentrated around the Bragg maxima. Although the discussion of the diffuse scattering was restricted to the case of identical domains, the introduction of a distribution of domain sizes does not influence the diffraction pattern essentially, as long as the fluctuation of sizes is small compared with the average volume of domain sizes and no strong correlation exists between domains of any size (size-independent random distribution).

The complete qualitative discussion of the diffraction pattern may be made by investigating the Fourier transform of (4.2.3.21a):

$$[L(\mathbf{H}) * T(\mathbf{H})] |\Delta F(\mathbf{H})|^2 |D(\mathbf{H})|^2. \quad (4.2.3.21b)$$

The first factor in (4.2.3.21b) describes the particle-size effect of a domain containing the influence of a surrounding strain field and the new structure of the domains precipitated from the bulk. $D(\mathbf{H})$ has its characteristic variation near the Bragg peaks (Figs. 4.2.3.2e, f), and is less important in between. For structure determination of domains, intensities near the Bragg peaks should be avoided. Note that equation (4.2.3.21b) may be used for measurements applying anomalous scattering in both the centric and the acentric case.

Solution of the diffraction problem. In equation (4.2.3.21b) $\Delta F(\mathbf{H})$ is replaced by its average

$$\langle \Delta F(\mathbf{H}) \rangle = \sum_{\mu} p_{\mu} \Delta F_{\mu}(\mathbf{H}),$$

where p_{μ} represents the *a priori* probability of a domain of type μ . This replacement becomes increasingly important if small clusters (domains) have to be considered. Applications of the formulae to Guinier–Preston zones are given by Guinier (1942) and Gerold (1954); a similar application to clusters of vacancies in spinels with an excess in Al_2O_3 was outlined by Jagodzinski & Haefner (1967).

Although refinement procedures are possible in principle, the number of parameters entering the diffraction problem becomes increasingly large if more clusters or domains (different sizes) have to be introduced. Another difficulty results from the large number of diffraction data which must be collected to perform a reliable structure determination. There is no need to calculate the first two terms in equation (4.2.3.20c) which do contribute to the sharp Bragg peaks only, because their intensity is simply described by the averaged structure factor $|\langle F(\mathbf{H}) \rangle|^2$. These terms may therefore be replaced by

$$|L(\mathbf{H})|^2 |\langle F(\mathbf{H}) \rangle|^2$$

with

$$|\langle F(\mathbf{H}) \rangle|^2 = \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2 \quad (4.2.3.21c)$$

where p_{μ} is the *a priori* probability of the structure factor $F_{\mu}(\mathbf{H})$. It should be emphasized here that (4.2.3.21c) is independent of the distribution function $d(\mathbf{r})$, or its Fourier transform $D(\mathbf{H})$.

(2) Periodic lamellar domains

Here $d(\mathbf{r})$ is one-dimensional, and can easily be calculated: a periodic array of two types of lamellae having the same basic lattice $l(\mathbf{r})$, but a different structure, is shown in Fig. 4.2.3.3. The size of the

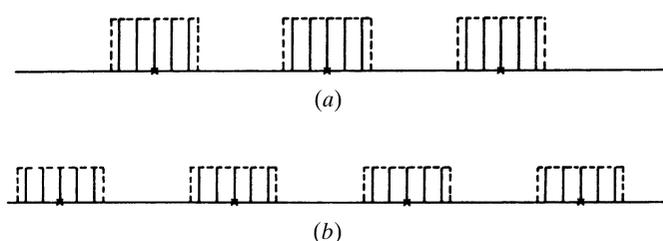


Fig. 4.2.3.3. Periodic array of domains consisting of two different atoms, represented by different heights. (a) Distribution of domain type 1, (b) distribution of domain type 2.

two types of lamellae may be different. The structure of the first domain type is given by a convolution with $F_1(\mathbf{r})$ (Fig. 4.2.3.3a) and that of the second domain type by $F_2(\mathbf{r})$ (Fig. 4.2.3.3b). Introducing $\langle F(\mathbf{r}) \rangle$ and $\Delta F(\mathbf{r})$, the structure in real space is described by:

$$\begin{aligned} & [l(\mathbf{r})b_1(\mathbf{r}) * d(\mathbf{r}) * F_1(\mathbf{r}) + [l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r}) * F_2(\mathbf{r}) \\ & = \{[l(\mathbf{r})b_1(\mathbf{r}) + l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r})\} * \langle F(\mathbf{r}) \rangle \\ & + [l(\mathbf{r})b_1(\mathbf{r}) - l(\mathbf{r})b_2(\mathbf{r}) * d(\mathbf{r}) * \Delta F(\mathbf{r}). \end{aligned} \quad (4.2.3.22a)$$

Obviously the first term in curly brackets in equation (4.2.3.22a) is no more than $l(\mathbf{r})$ itself and $d(\mathbf{r})$ is strictly periodic. $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ are box functions, mutually displaced by $\pm(n_1 + n_2)/2$ unit cells in the \mathbf{c} direction [n_1, n_2 are the numbers of cells covered by $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$, respectively].

Fourier transformation of equation (4.2.3.22a) yields

$$L(\mathbf{H}) \langle F(\mathbf{H}) \rangle + \{L(\mathbf{H}) * [B_1(\mathbf{H}) - B_2(\mathbf{H})]\} D(\mathbf{H}) \Delta F(\mathbf{H}). \quad (4.2.3.22b)$$

The first term in equation (4.2.3.22b) gives the normal sharp reflections of the average structure, while the second describes superlattice reflections [sublattice $L_s(\mathbf{H}) = D(\mathbf{H})$ in reciprocal space], multiplied by $\Delta F(\mathbf{H})$ and another ‘structure factor’ generated by the convolution of the reciprocal lattice $L(\mathbf{h})$ with $[B_1(\mathbf{H}) - B_2(\mathbf{H})]$ (*cf.* Fig. 4.2.3.3b). Since the centres of $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ are mutually displaced, the expression in square brackets includes extinctions if $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$ represent boxes equal in size. These extinctions are discussed below. It should be pointed out that $L_s(\mathbf{H})$ and its Fourier transform $l_s(\mathbf{r})$ are commensurate with the basic lattice, as long as no change of the translation vector at the interface of the lamellae occurs. Obviously, $L_s(\mathbf{H})$ becomes incommensurate in the general case of a slightly distorted interface. Considerations of this kind play an important role in the discussion of modulated structures.

No assumption has been made so far for the position of the interface. This point is meaningless only in the case of a strictly periodic array of domains (no diffuse scattering). Therefore it seems to be convenient to introduce two basic vectors parallel to the interface in real space which demand a new reciprocal vector perpendicular to them defined by $(\mathbf{a}' \times \mathbf{b}')/V'$, where \mathbf{a}' , \mathbf{b}' are the new basic vectors and V' is the volume of the supercell. As long as the new basic vectors are commensurate with the original lattice, the direction of the new reciprocal vector \mathbf{c}^* , perpendicular to \mathbf{a}' , \mathbf{b}' , passes through the Bragg points of the original reciprocal lattice and the reciprocal lattice of the superlattice remains commensurate as long as V' is a multiple of V ($V' = mV$, $m = \text{integer}$). Since the direction of \mathbf{c} is arbitrary to some extent, there is no clear rule about the assignment of superlattice reflections to the original Bragg peaks. This problem becomes very important if extinction rules of the basic lattice and the superlattice have to be described together.

4. DIFFUSE SCATTERING AND RELATED TOPICS

Example. We consider a b.c.c. structure with two kinds of atoms (1, 2) with a strong tendency towards superstructure formation (CsCl-type ordering). According to equations (4.2.3.21b,c) and (4.2.3.22b) we obtain, in the case of negligible short-range order, the following expressions for sharp and diffuse scattering (c = concentration):

$$I_s = |cF_1(\mathbf{H}) + (1-c)F_2(\mathbf{H})|^2 \quad \text{for } h+k+l = 2n$$

$$I_d = c(1-c)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2 \quad \text{elsewhere.}$$

With increasing short-range order the sharp reflections remain essentially unaffected, while the diffuse ones concentrate into diffuse maxima at \mathbf{h} with $h+k+l = 2n+1$. This process is treated more extensively below. As long as the domains exhibit no clear interface, it is useful to describe the ordering process with the two possible cell occupations of a pair of different atoms; then contributions of equal pairs may be neglected with increasing short-range order. Now the two configurations 1, 2 and 2, 1 may be given with the aid of the translation $\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. Hence the two structure factors are

$$F_1 \text{ and } F_2 = F_1 \exp\{\pi i(h+k+l)\}.$$

Since both structure factors occur with the same probability, the equations for sharp and diffuse reflections become

$$I_s = \frac{1}{4}|F_1(\mathbf{H})|^2 [1 + \exp\{\pi i(h+k+l)\}]^2$$

$$I_d = \frac{1}{4}|F_1(\mathbf{H})|^2 [1 - \exp\{\pi i(h+k+l)\}]^2.$$

It is well recognized that no sharp reflections may occur for $h+k+l = 2n+1$, and the same holds for the diffuse scattering if $h+k+l = 2n$. This extinction rule for diffuse scattering is due to suppression of contributions of equal pairs. The situation becomes different for lamellar structures. Let us first consider the case of lamellae parallel to (100). The ordered structure is formed by an alternating sequence of monoatomic layers, consisting of atoms of types 1 and 2, respectively. Hence, the interface between two neighbouring domains is a pair of equal layers 1,1 or 2,2 which are not equivalent. Each interface of type 1 (2) may be described by an inserted layer of type 1 (2), and the chemical composition differs from 1:1 if one type of interface is preferred. Since the contribution of equal pairs has been neglected in deriving the extinction rule of diffuse scattering (see above) this rule is no longer valid. Because of the lamellar structure the diffuse intensity is concentrated into streaks parallel to (00 l). Starting from the diffuse maximum (010), the diffuse streak passes over the sharp reflection 011 to the next diffuse one 012 *etc.*, and the extinction rule is violated as long as one of the two interfaces is predominant. Hence, the position of the interface determines the extinction rule in this orientation.

A completely different behaviour is observed for lamellae parallel to (110). This structure is described by a sequence of equal layers containing 1 and 2 atoms. The interface between two domains (exchange of the two different atoms) is now nothing other than the displacement parallel to the layer of the original one in the ordered sequence. Calculation of the two structure factors would involve displacements $\pm\frac{1}{2}(\mathbf{a} - \mathbf{b})$. Starting from the diffuse reflection 001, the diffuse streak parallel to (HH0) passes through (111), (221), (331), . . . ; *i.e.* through diffuse reflections only. On the other hand, rows (HH2) going through (002), (112), (222), . . . do not show any diffuse scattering. Hence, we have a new extinction rule for diffuse scattering originating from the orientation of interfaces. This fact is rather important in structure determination. For various reasons, lamellar interfaces show a strong tendency towards a periodic arrangement. In diffraction the diffuse streak then concentrates into more or less sharp superstructure reflections. These are not observed on those rows of the reciprocal lattice which are free from diffuse scattering. The same extinction law is not valid

in the case of the (100) orientation of the interfaces. Summarizing, we may state that three types of extinction rules have to be considered:

- (a) Normal extinctions for the average structure.
- (b) Extinction of the difference structure factors for diffuse scattering.
- (c) Extinctions caused by the ordering process itself.

(3) *Lamellar system with two different structures, where $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$ do not obey any systematic extinction law*

The convolution of the second term in equation (4.2.3.22b) (cf. Fig. 4.2.3.3) may be represented by a convolution of the Fourier transform of a box function $B_1(\mathbf{H})$ with the reciprocal superlattice. Since $B_1(\mathbf{H})$ is given by $\sin(\pi m_s H)/(\pi H)$, where m_s = number of cells of the supercell, the reader might believe that the result of the convolution may easily be determined quantitatively: this assumption is not correct because of the slow convergence of $B_1(\mathbf{H})$. The systematic coincidences of the maxima, or minima, of $B_1(\mathbf{H})$ with the points of the superlattice in the commensurate case cause considerable changes in intensities especially in the case of a small thickness of the domains. For this reason an accurate calculation of the amplitudes of satellites is necessary (Jagodzinski & Penzkofer, 1981):

(a) Bragg peaks of the basic lattice

$$I \sim |\langle F(\mathbf{H}) \rangle|^2; \quad (4.2.3.23a)$$

(b) satellites: $\nu = 2n$ (n = integer except 0)

$$I \sim |2 \sin \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2; \quad (4.2.3.23b)$$

(c) satellites: $\nu = 2n + 1$

$$I \sim |2 \cos \pi \nu C / [\sin \pi \nu / (N_1 + N_2)] \Delta F(\mathbf{H})|^2. \quad (4.2.3.23c)$$

ν = order of satellites, $C = \frac{1}{2}(N_1 - N_2)/(N_1 + N_2)$, N_1, N_2 = number of cells within $b_1(\mathbf{r})$ and $b_2(\mathbf{r})$, respectively.

Obviously, there is again a systematic extinction rule for even satellites if $N_1 = N_2$.

Equation (4.2.3.23b) indicates an increasing intensity of first even-order satellites with increasing C . Intensities of first even and odd orders become nearly equal if $N_2 \simeq \frac{1}{2}N_1$. Smaller values of N_2 result in a decrease of intensities of both even and odd orders (no satellites if $N_2 = 0$). The denominators in equations (4.2.3.23b,c) indicate a decrease in intensity with increasing order of satellites. The quantitative behaviour of the intensities needs a more detailed discussion of the numerator in equations (4.2.3.23a,b) with increasing order of satellites. Obviously, there are two kinds of extinction rules to be taken into account: systematic absences for the various orders of satellites, and the usual extinctions for $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$. Both have to be considered separately in order to arrive at reliable conclusions. This different behaviour of the superlattice reflections (satellites) and that of the basic lattice may well be represented by a multi-dimensional group-theoretical representation as has been shown by de Wolff (1974), Janner & Janssen (1980), de Wolff *et al.* (1981), and others.

(4) *Non-periodic system (qualitative discussion)*

Following the discussion of equations (4.2.3.21) one may conclude that the fluctuations of domain sizes cause a broadening of satellites, if the periodic distribution function has to be replaced by a statistical one. In this case the broadening effect increases with the order of satellites. The intensities, however, are completely determined by the distribution function and can be estimated by calculating the intensities of the perfectly ordered array, as approximated by the distribution function.

A careful check of $\langle F(\mathbf{H}) \rangle$ and $\Delta F(\mathbf{H})$ in equations (4.2.3.23) shows that the position of the interface plays an important role for

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the intensities of satellites. Since this position determines the origin of the unit cells in the sublattice, we have to choose this origin for the calculation of $F(\mathbf{H})$ and $\Delta F(\mathbf{H})$. This involves phase factors which are meaningless for integral values of \mathbf{H} , (i) if the average $\langle F(\mathbf{H}) \rangle$ refers to different structures with arbitrary origin, or (ii), which is important for practical cases, where no change occurs in the origin of related structures for neighbouring domains which are bound to an origin by general convention (e.g. a centre of symmetry). This statement is no longer true for non-integral values of \mathbf{H} which are needed for the calculation of intensities of satellites. The intensities of satellites become different for different positions of the interface, even in the absence of a relative displacement between neighbouring domains with respect to an origin by convention. This statement may be extended to non-periodic distribution functions. Consequently, one may conclude that the study of diffuse scattering yields information on the interfacial scattering. For slightly different structures at the interface two cases are important:

(i) the two structures are related by symmetry (e.g. by a twin law); and

(ii) the difference between the two structures cannot be described by a symmetry operation.

In structures based on the same sublattice, the first case seems to be more important, because two different structures with the same sublattice are improbable. In the first case there is an identical sublattice if the symmetry operation in question does not influence the plane of intergrowth, e.g. a mirror plane should coincide with the plane of intergrowth. Since we have two inequivalent mirror planes in any sublattice, there are two such planes. It is assumed that no more than one unit cell of both domains at the interface has a slightly different structure without any change of geometry of the unit cell, and the number of unit cells is equal because of the equivalence of both domain structures (twins). Fig. 4.2.3.4(a) shows a picture of this model; Figs. 4.2.3.4(b), (c) explain that this structure may be described by two contributions:

(i) The first term is already given by equation (4.2.3.23) for $N_1 = N_2$, consequently odd orders of satellites only are observed.

(ii) The second term may be described by a superlattice containing $2N_1$ cells with an alternating arrangement of interfaces, correlated by the relevant plane of symmetry.

In real space the second term may be constructed by convolution of the one-dimensional superlattice with two difference structures displaced by $\mp N_1/2$ units of the sublattice; its Fourier transformation yields

$$L_s(\mathbf{H})\{\Delta F_i(\mathbf{H}) \exp\{2\pi i N_1 H/2\} + \Delta F'_i(\mathbf{H}) \exp\{-2\pi i N_1 H/2\}\}, \quad (4.2.3.24)$$

where $\Delta F_i, \Delta F'_i$ correspond to the Fourier transforms of the contributions shown in Fig. 4.2.3.4(c). Since $H = \nu/N_1$ there are alternating contributions to the ν th satellite, which may be calculated more accurately by taking into account the symmetry operations. The important difference between equations (4.2.3.23) and (4.2.3.24) is the missing decrease in intensity with increasing order of satellites. Consequently one may conclude that the interface contributes to low- and high-order satellites as well, but its influence prevails for high-order satellites. Similar considerations may be made for two- and three-dimensional distributions of domains. A great variety of extinction rules may be found depending on the type of order approximated by the distribution under investigation.

(5) *Two kinds of lamellar domains with variable size distribution*

Obviously the preceding discussion of the diffuse scattering from domains is restricted to more or less small fluctuations of domain sizes. This is specifically valid if the most probable domain size

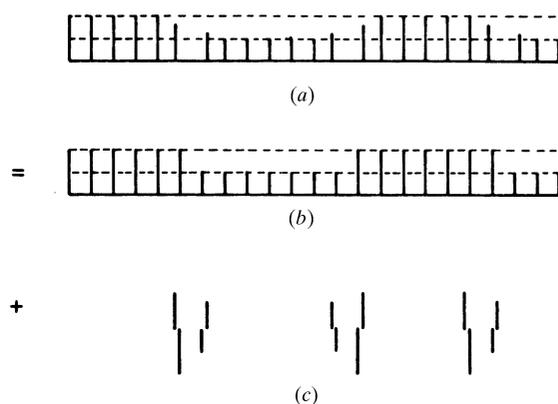


Fig. 4.2.3.4. Influence of distortions at the boundary of domains, and separation into two parts; for discussion see text.

does not differ markedly from the average size. The condition is violated in the case of order-disorder phenomena. It may happen that the smallest ordered area is the most probable one, although the average is considerably larger. This may be shown for a lamellar structure of two types of layers correlated by a (conditional) pair probability $p_{\mu\mu'}(\mathbf{1})$. As shown below, a pair at distance \mathbf{m} occurs with the probability $p_{\mu}p_{\mu'}(\mathbf{m})$ which may be derived from the pair-probability of nearest neighbours $p_{\mu}p_{\mu'}(\mathbf{1})$. (In fact only one component of vector \mathbf{m} is relevant in this context.) The problem will be restricted to two kinds of layers ($\mu, \mu' = 1, 2$). Furthermore, it will be symmetric in the sense that the pair probabilities obey the following rules

$$p_{11}(\mathbf{m}) = p_{22}(\mathbf{m}), \quad p_{12}(\mathbf{m}) = p_{21}(\mathbf{m}). \quad (4.2.3.25)$$

It may be derived from equation (4.2.3.25) that the *a priori* probabilities p_{μ} of a single layer are $\frac{1}{2}$ and

$$p_{11}(\mathbf{0}) = p_{22}(\mathbf{0}) = 1, \quad p_{12}(\mathbf{0}) = p_{21}(\mathbf{0}) = 0.$$

With these definitions and the general relation

$$p_{11}(\mathbf{m}) + p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) + p_{21}(\mathbf{m}) = 1$$

the *a priori* probability of a domain containing m layers of type 1 may be calculated with the aid of $p_{11}(\mathbf{1})$ [$0 \leq p_{11}(\mathbf{1}) \leq 1$]:

$$p_{\mu} = \frac{1}{2} p_{11}(\mathbf{1})^{m-1} [1 - p_{11}(\mathbf{1})]. \quad (4.2.3.26)$$

Hence the most probable size of domains is a single layer because a similar relation holds for layers of type 2. Since the average thickness of domains is strongly dependent on $p_{11}(\mathbf{1})$ [infinite for $p_{11}(\mathbf{1}) = 1$, and one layer for $p_{11}(\mathbf{1}) = 0$] it may become very large in the latter case. Consequently there are extremely large fluctuations if $p_{11}(\mathbf{1})$ is small, but different from zero.

It may be concluded from equation (4.2.3.26) that the function $p_{11}(\mathbf{m})$ decreases monotonically with increasing \mathbf{m} , approaching $\frac{1}{2}$ with $\mathbf{m} \rightarrow \infty$. Apparently this cannot be true for a finite crystal if $p_{11}(\mathbf{m})$ is unity (structure of two types of domains) or zero (superstructure of alternating layers). In either case the crystal should consist of a single domain of type 1 or 2, or one of the possible superstructures 1212 . . . , 2121 . . . , respectively. Hence one has to differentiate between long-range order, where two equivalent solutions have to be considered, and short-range order, where $p_{11}(\mathbf{m})$ approaches the *a priori* probability $\frac{1}{2}$ for large m . This behaviour of $p_{11}(\mathbf{m})$ and $p_{12}(\mathbf{m})$, which may also be expressed by equivalent correlation functions, is shown in Figs. 4.2.3.5(a) (short-range order) and 4.2.3.5(b) (long-range order). $p_{11}(\mathbf{m})$ approaches $\frac{1}{2} + s$ for large m with $s = 0$ in the case of short-range order, while $p_{12}(\mathbf{m})$ becomes $\frac{1}{2} - s$. Obviously a strict correlation between $p_{11}(\mathbf{1})$ and s exists which has to be calculated. For a qualitative

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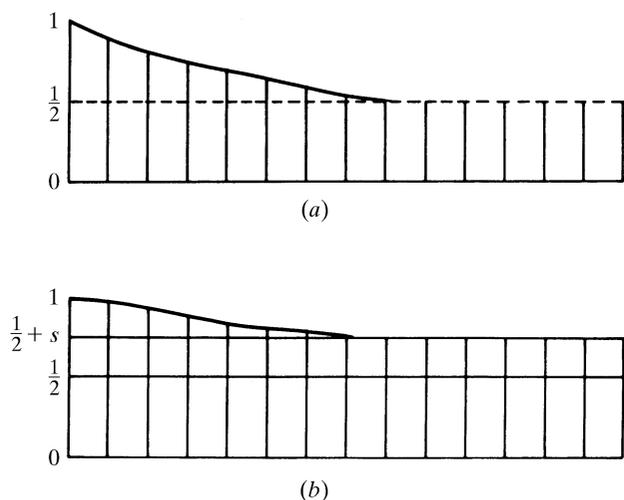


Fig. 4.2.3.5. Typical distributions of mixed crystals (unmixing): (a) upper curve: short-range order only; (b) lower curve: long-range order.

interpretation of the diffraction pictures this correlation may be derived from the diffraction pattern itself. The $p_{\mu\mu'}(\mathbf{m})$ are separable into a strictly periodic and a monotonically decreasing term approaching zero in both cases. This behaviour is shown in Figs. 4.2.3.6(a), (b). The periodic term contributes to sharp Bragg scattering. In the case of short-range order the symmetry relations given in equation (4.2.3.25) are valid. The convolution in real space yields with factors $t(\mathbf{r})$ (equations 4.2.3.21):

$$\begin{aligned} & \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{11}(\mathbf{m})\right]*F_1(\mathbf{r})*F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{12}(\mathbf{m})\right]*F_1(\mathbf{r})*F_2(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{21}(\mathbf{m})\right]*F_2(\mathbf{r})*F_1(-\mathbf{r}) \\ & + \frac{1}{2}t(\mathbf{r})\left[\sum_{\mathbf{m}}\delta(\mathbf{r}+\mathbf{m})p'_{22}(\mathbf{m})\right]*F_2(\mathbf{r})*F_2(-\mathbf{r}), \end{aligned}$$

where $p'_{\mu\mu'}(\mathbf{m})$ are factors attached to the δ functions:

$$\begin{aligned} p'_{11}(\mathbf{m}) &= p_{11}(\mathbf{m}) - \frac{1}{2} = p'_{22}(\mathbf{m}) \\ p'_{12}(\mathbf{m}) &= p'_{21}(\mathbf{m}) = -p'_{11}(\mathbf{m}). \end{aligned}$$

The positive sign of n in the δ functions results from the convolution with the inverted lattice [cf. Patterson (1959, equation 32)]. Fourier

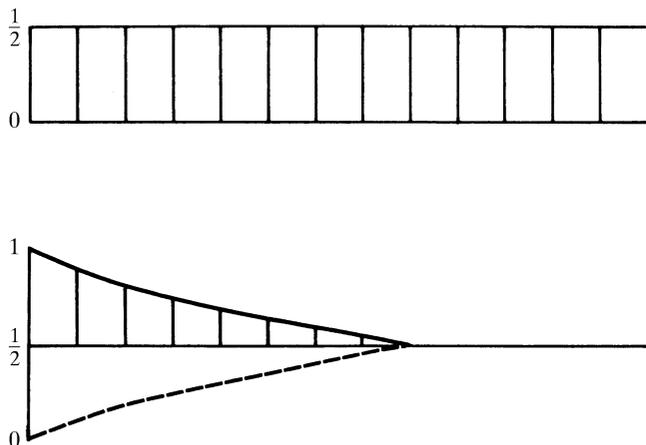


Fig. 4.2.3.6. Decomposition of Fig. 4.2.3.5(a) into a periodic and a rapidly convergent part.

transformation of the four terms given above yields the four corresponding expressions (μ, μ'):

$$\frac{1}{2}[T(\mathbf{H}) * \sum_{\mathbf{m}} p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i\mathbf{H} \cdot \mathbf{m}\}]F_{\mu}(\mathbf{H})F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27a)$$

Now the summation over \mathbf{m} may be replaced by an integral if the factor $l(\mathbf{m})$ is added to $p'_{\mu\mu'}(\mathbf{m})$, which may then be considered as the smoothest continuous curve passing through the relevant integer values of \mathbf{m} :

$$\sum \rightarrow \int l(\mathbf{m})p'_{\mu\mu'}(\mathbf{m}) \exp\{-2\pi i\mathbf{H} \cdot \mathbf{m}\} d\mathbf{m}$$

since both $l(\mathbf{m})$ and $p'_{\mu\mu'}(\mathbf{m})$ are symmetric in our special case we obtain

$$\sum = L(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H}).$$

Insertion of the sum in equation (4.2.3.27a) results in

$$\frac{1}{2}[L(\mathbf{H}) * T(\mathbf{H}) * P'_{\mu\mu'}(\mathbf{H})]F_{\mu}(\mathbf{H})F_{\mu'}^+(\mathbf{H}). \quad (4.2.3.27b)$$

Using all symmetry relations for $p'_{\mu\mu'}(\mathbf{m})$ and $P'_{\mu\mu'}(\mathbf{H})$, respectively, we obtain for the diffuse scattering after summing over μ, μ'

$$I_d \approx [L(\mathbf{H}) * T(\mathbf{H}) * P'_{11}(\mathbf{H})]|\Delta F(\mathbf{H})|^2 \quad (4.2.3.28)$$

with $\Delta F(\mathbf{H}) = \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]$.

It should be borne in mind that $P'_{11}(\mathbf{H})$ decreases rapidly if $p'_{11}(\mathbf{r})$ decreases slowly and *vice versa*. It is interesting to compare the different results from equations (4.2.3.21b) and (4.2.3.28). Equation (4.2.3.28) indicates diffuse maxima at the positions of the sharp Bragg peaks, while the multiplication by $D(\mathbf{H})$ causes satellite reflections in the neighbourhood of Bragg maxima. Both equations contain the factor $|\Delta F(\mathbf{H})|^2$ indicating the same influence of the two structures. More complicated formulae may be derived for several cell occupations. In principle, a result similar to equation (4.2.3.28) will be obtained, but more interdependent correlation functions $p_{\mu\mu'}(\mathbf{r})$ have to be introduced. Consequently, the behaviour of diffuse intensities becomes more differentiated in so far as all $p'_{\mu\mu'}(\mathbf{r})$ are now correlated with the corresponding $\Delta F_{\mu}(\mathbf{r}), \Delta F_{\mu'}(-\mathbf{r})$. Hence the method of correlation functions becomes increasingly ineffective with increasing number of correlation functions. Here the cluster method seems to be more convenient and is discussed below.

(6) *Lamellar domains with long-range order: tendency to exsolution*

The Patterson function of a disordered crystal exhibiting long-range order is shown in Fig. 4.2.3.5(b). Now $p_{11}(\infty)$ converges against $\frac{1}{2} + s$, the *a priori* probability changes correspondingly. Since $p_{12}(\infty)$ becomes $\frac{1}{2} - s$, the symmetry relation given in equation (4.2.3.25) is violated: $p_{11}(\mathbf{r}) \neq p_{22}(\mathbf{r})$ for a finite crystal; it is evident that another crystal shows long-range order with the inverted correlation function, $p_{22}(\infty) = \frac{1}{2} + s$, $p_{21}(\infty) = \frac{1}{2} - s$, respectively, such that the symmetry $p_{11}(\mathbf{r}) = p_{22}(\mathbf{r})$ is now valid for an assembly of finite crystals only. According to Fig. 4.2.3.5(b) there is a change in the intensities of the Bragg peaks.

$$\begin{aligned} I_1 &\sim |(\frac{1}{2} + s)F_1(\mathbf{H}) + (\frac{1}{2} - s)F_2(\mathbf{H})|^2 \\ I_2 &\sim |(\frac{1}{2} + s)F_2(\mathbf{H}) + (\frac{1}{2} - s)F_1(\mathbf{H})|^2, \end{aligned} \quad (4.2.3.29)$$

where I_1, I_2 represent the two solutions discussed for the assembly of crystals which have to be added with the probability $\frac{1}{2}$; the intensities of sharp reflections become

$$I = (I_1 + I_2)/2. \quad (4.2.3.30)$$

Introducing equation (4.2.3.29) into (4.2.3.30) we obtain

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$$I \sim \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 + s^2[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.31a)$$

$s = 0$ corresponds to the well known behaviour of sharp reflections, $s = \frac{1}{2}$ (maximum long-range order) gives

$$I \sim \frac{1}{2}[|F_1(\mathbf{H})|^2 + |F_2(\mathbf{H})|^2]. \quad (4.2.3.31b)$$

This result reveals some difficulties for structure determination of the averaged structure as long as s is different from zero or $\frac{1}{2}$, since in the former case the use of integrated sharp Bragg intensities yields a correct average structure. If $s = \frac{1}{2}$, a correct structure determination can only be performed with a refinement allowing for an incoherent superposition of two different structures. Having subtracted all periodic contributions to $p_{\mu\mu'}(\mathbf{r})$, new functions which describe the remaining non-periodic parts have to be introduced (Fig. 4.2.3.6b). In order to obtain a clear overview of intensities, $p'_{\mu\mu'}(\mathbf{r})$ is again defined:

$$p'_{\mu\mu'}(\mathbf{r}) = cp_{\mu\mu'}(\mathbf{r}) - p_{\mu\mu'}(\infty),$$

where c should be chosen such that $p_{\mu\mu'}(\mathbf{0}) = 1$. By this definition a very simple behaviour of the diffuse scattering is obtained:

$$\begin{aligned} p'_{11}(\mathbf{r}) &: \frac{1}{2} - s; & p'_{12}(\mathbf{r}) &: -(\frac{1}{2} - s); \\ p'_{22}(\mathbf{r}) &: \frac{1}{2} + s; & p'_{21}(\mathbf{r}) &: -(\frac{1}{2} + s). \end{aligned}$$

With the definitions introduced above it is found that:

$$p'_{11}(\mathbf{r}) = p'_{22}(\mathbf{r}).$$

The diffuse scattering is given by:

$$I_d(\mathbf{H}) = (\frac{1}{4} - s^2)|F_1(\mathbf{H}) - F_2(\mathbf{H})|^2 [P'_{11}(\mathbf{H}) * L(\mathbf{H})]. \quad (4.2.3.32)$$

Since equation (4.2.3.32) is symmetrical with respect to an interchange of F_1 and F_2 , the same result is obtained for I_2 . Diffuse reflections occur in the positions of the sharp ones; the integrated intensities of sharp and diffuse reflections are independent of the special shape of $P'_{11}(\mathbf{H})$: $p_{11}(\mathbf{0}) = 1$; hence

$$1 = \int P'_{11}(\mathbf{H}) \exp\{2\pi i \mathbf{0} \cdot \mathbf{H}\} d\mathbf{H} = \int P'_{11}(\mathbf{H}) d\mathbf{H}.$$

(7) *Lamellar domains with long-range order: tendency to superstructure*

So far it has been tacitly assumed that the crystal shows a preference for equal neighbours. If there is a reversed tendency (pairs of unequal neighbours are more probable) the whole procedure outlined above may be repeated as shown in Fig. 4.2.3.7 for the one-dimensional example. With the same probability of an unlike pair as used for the equal pair in the preceding example, the order process approaches an alternating structure such that the even-order neighbours have the same pair probabilities, while the odd ones are complementary for equal pairs (Fig. 4.2.3.7). In order to calculate intensities, it is necessary to introduce a new lattice with the doubled lattice constant and the corresponding reciprocal lattice with $b^{*'} = b^*/2$. In order to describe the probability $p_{\mu\mu'}(\mathbf{r})$, one has to introduce two lattices in real space – the normal lattice with the

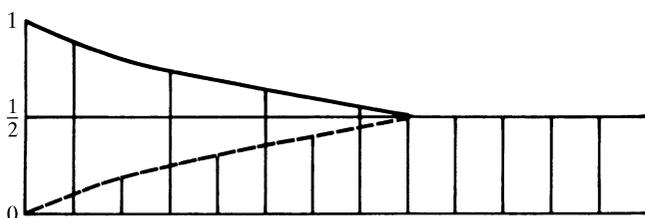


Fig. 4.2.3.7. The same distribution (cf. Fig. 4.2.3.5) in the case of superstructure formation.

undisplaced origin and the displaced one. Fourier transformation of the new functions yields the following very similar results:

Sharp Bragg reflections

(a) $k' = \text{even}$

$$I = \frac{1}{2}[F_1(\mathbf{H}) + F_2(\mathbf{H})]^2 \quad (4.2.3.33a)$$

(b) $k' = \text{odd}$

$$I = s^2 \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2 \quad (4.2.3.33b)$$

Diffuse reflections

(c) $k' = \text{odd}$

$$I = (\frac{1}{4} - s^2) \frac{1}{2}[F_1(\mathbf{H}) - F_2(\mathbf{H})]^2. \quad (4.2.3.33c)$$

Obviously, there is a better situation for determination of the averaged structure which may be performed without any difficulty, regardless of whether s is different from zero or not. For this purpose even reflections (or reflections in the old setting) may be used. The inclusion of odd reflections in the structure determination of the superstructure is also possible if convenient \mathbf{H} -independent scaling factors are introduced in order to compensate for the loss in intensity which is unavoidable for the integration of the diffuse scattering.

A few comments should be made on the physical meaning of the formulae derived above. All formulae may be applied to the general three-dimensional case, where long-range and short-range order is a function of the relevant thermodynamical parameters. In practice, long-range order will never be realized in a real crystal consisting of mosaic blocks which may behave as small subunits in order-disorder transitions. Another reason to assume partly incoherent areas in single crystals is the presence of possible strains or other distortions at the interfaces between domains which should cause a decrease of the averaged areas of coherent scattering. All these effects may lead to diffuse scattering in the neighbourhood of Bragg peaks, similar to the diffuse scattering caused by domain structures. For this reason an incoherent treatment of domains is probably more efficient, although considerable errors in intensity measurements may occur. A very careful study of line profiles is generally useful in order to decide between the various possibilities.

(8) *Order-disorder in three dimensions*

Correlation functions in three dimensions may have very complicated periodicities; hence a careful study is necessary as to whether or not they may be interpreted in terms of a superlattice. If so, extinction rules have to be determined in order to obtain information on the superspace group. In the literature these are often called modulated structures because a sublattice, as determined by the basic lattice, and a superlattice may well be defined in reciprocal space: reflections of a sublattice including (000) are formally described by a multiplication by a lattice having larger lattice constants (superlattice) in reciprocal space; in real space this means a convolution with the Fourier transform of this lattice (sublattice). In this way the averaged structure is generated in each of the subcells (superposition or 'projection' of all subcells into a single one). Obviously, the Patterson function of the averaged structure contains little information in the case of small subcells. Hence it is advisable to include the diffuse scattering of the superlattice reflections at the beginning of any structure determination.

N subcells in real space are assumed, each of them representing a kind of a complicated 'atom' which may be equal by translation or other symmetry operation. Once a superspace group has been determined, the usual extinction rules of space groups may be applied, remembering that the 'atoms' themselves may have systematic extinctions. Major difficulties arise from the existence of different symmetries of the subgroup and the supergroup. Since the symmetry of the supergroup is lower in general, all missing

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symmetry elements may cause domains, corresponding to the missing symmetry element: translations cause antiphase domains in their generalized sense, other symmetry elements cause twins generated by rotations, mirror planes or the centre of symmetry. If all these domains are small enough to be detected by a careful study of line profiles, using diffraction methods with a high resolution power, the structural study may be facilitated by a reasonable explanation of scaling factors to be introduced for groups of reflections affected by the possible domain structures.

(9) Density modulations

A density modulation of a structure in real space leads to pairs of satellites in reciprocal space. Each main reflection is accompanied by a pair of satellites in the directions $\mp\Delta\mathbf{H}$ with phases $\mp 2\pi\varphi$. The reciprocal lattice may then be written in the following form ($0 \leq \alpha \leq 1$):

$$L(\mathbf{H}) + \frac{\alpha}{2}L(\mathbf{H} + \Delta\mathbf{H}) \exp\{2\pi i\Phi\} + \frac{\alpha}{2}L(\mathbf{H} - \Delta\mathbf{H}) \exp\{2\pi i(-\Phi)\}.$$

Fourier transformation yields

$$l(\mathbf{r}) \left[1 + \frac{\alpha}{2} \exp\{2\pi i(\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} + \frac{\alpha}{2} \exp\{-2\pi i(\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)\} \right] = l(\mathbf{r}) [1 + \alpha \cos(2\pi\Delta\mathbf{H} \cdot \mathbf{r} + \Phi)]. \quad (4.2.3.34)$$

Equation (4.2.3.34) describes the lattice modulated by a harmonic density wave. Since phases cannot be determined by intensity measurements, there is no possibility of obtaining any information on the phase relative to the sublattice. From (4.2.3.34) it is obvious that the use of higher orders of harmonics does not change the situation. If $\Delta\mathbf{H}$ is not rational such that $n\Delta\mathbf{H}$ ($n = \text{integer}$) does not coincide with a main reflection in reciprocal space, the modulated structure is incommensurate with the basic lattice, and the phase of the density wave becomes meaningless. The same is true for the relative phases of the various orders of harmonic modulations of the density. This uncertainty even remains valid for commensurate density modulations of the sublattice, because coinciding higher-order harmonics in reciprocal space cause the same difficulty; higher-order coefficients cannot uniquely be separated from lower ones, consequently structure determination becomes impossible unless phase-determination methods are applied. Fortunately, density modulations of pure harmonic character are impossible for chemical reasons; they may be approximated by disorder phenomena for the averaged structure only. If diffuse scattering is taken into account the situation is changed considerably: A careful study of the diffuse scattering alone, although difficult in principle, will yield the necessary information about the relative phases of density waves (Korekawa, 1967).

(10) Displacement modulations

Displacement modulations are more complicated, even in a primitive structure. The Fourier transform of a longitudinal or a transverse displacement wave has to be calculated and this procedure does not result in a function of similar simplicity. A set of satellites is generated whose amplitudes are described by Bessel functions of ν th order, where ν represents the order of the satellites. With α as amplitude of the displacement wave the intensity of the satellites increases with the magnitude of the product $H\alpha$. This means that a single harmonic displacement causes an infinite number of satellites. They may be unobservable at low diffraction angles as long as the amplitudes are small. If the displacement

modulation is incommensurate there are no coincidences with reflections of the sublattice. Consequently, the reciprocal space is completely covered with an infinite number of satellites, or, in other words, with diffuse scattering. This is a clear indication that incommensurate displacement modulations belong to the category of disordered structures. Statistical fluctuations of amplitudes of the displacement waves cause additional diffuse scattering, regardless of whether the period is commensurate or incommensurate (Overhauser, 1971; Axe, 1980). Fluctuations of 'phases' (= periods) cause a broadening of satellites in reciprocal space, but no change of their integrated intensities as long as the changes are not correlated with fluctuation periods. The broadening of satellite reflections increases with the order of satellites and $(\mathbf{H} \cdot \mathbf{a})$. Obviously, there is no fundamental difference in the calculation of diffuse scattering with an ordered supercell of sufficient size.

The use of optical transforms has been revived recently, although its efficiency is strongly dependent on the availability of a useful computer program capable of producing masks for optical diffraction. An atlas of optical transforms is available (Wooster, 1962; Harburn *et al.*, 1975), but the possibility cannot be excluded that the diffuse scattering observed does not fit well into one of the diffraction pictures shown. Yet one of the major advantages of this optical method is the simple experimental setup and the high brilliance owing to the use of lasers. This method is specifically useful in disordered molecular structures where only a few orientations of the molecules have to be considered. It should be borne in mind, however, that all optical masks must correspond to projections of the disorder model along one specific direction which generates the two-dimensional diffraction picture under consideration. An important disadvantage is caused by the difficulty in simulating the picture of an atom. This situation may be improved by using computer programs with a high-resolution matrix printer representing electron densities by point densities of the printer. This latter method seems to be very powerful because of the possibility of avoiding 'ghosts' in the diffraction picture.

4.2.3.2. Guideline to solve a disorder problem

Generally, structure determination of a disordered crystal should start in the usual way by solving the average structure. The effectiveness of this procedure strongly depends on the distribution of integrated intensities of sharp and diffuse reflections. In cases where the integrated intensities of Bragg peaks is predominant, the maximum information can be drawn from the averaged structure. The observations of fractional occupations of lattice sites, split positions and anomalous temperature factors are indications of the disorder involved. Since these aspects of disorder phenomena in the averaged structure may be interpreted very easily, a detailed discussion of this matter is not given here (see any modern textbook of X-ray crystallography).

Difficulties may arise from the intensity integration which should be carried out using a high-resolution diffraction method. The importance of this may be understood from the following argument. The averaged structure is determined by the coherent superposition of different structure factors. This interpretation is true if there is a strictly periodic subcell with long-range order which allows for a clear separation of sharp and diffuse scattering. There are important cases, however, where this procedure cannot be applied without loss of information.

(a) The diffuse scattering is concentrated near the Bragg peaks for a large number of reflections. Because of the limited resolution power of conventional single-crystal methods the separation of sharp and diffuse scattering is impossible. Hence, the conventional study of integrated intensities does not really lead to an averaged structure. In this case a refinement should be tried using an incoherent superposition of different structure factors. Application

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of this procedure is subject to conditions which have to be checked very carefully before starting the refinement: first, it is necessary to estimate the amount of diffuse scattering not covered by intensity integration of the 'sharp' reflections. Since loss in intensity, hidden in the background scattering, is underestimated very frequently, it should be checked whether nearly coinciding sharp and diffuse maxima are modulated by the same structure factor. It may be difficult to meet this condition in some cases; *e.g.* this condition is fulfilled for antiphase domains, but the same is not true for twin domains.

(b) The concentration of diffuse maxima near Bragg peaks is normally restricted to domain structures with a strictly periodic sublattice. Cases deviating from this rule are possible. Since they are rare, they are omitted here. Even structures with small deviations from the average structure do not lead to structure factors for diffuse scattering which are proportional to that of the average structure. This has been shown in the case of a twin structure correlated by a mirror plane where the reflections of a zone only have equal structure factors (Cowley & Au, 1978). This effect causes even more difficulties for orthogonal lattices where the two twins have reflections in exactly the same positions, although differing in their structure factors. In this particular case, the incoherent or coherent treatment in refinements may be seriously hampered by strains originating from the boundary. Unsatisfactory refinements may be explained in this way but this does not improve their reliability.

The integrated intensity of any structure is independent of atomic positions if the atomic form factors remain unchanged by structural fluctuations. Small deviations of atomic form factors owing to electron-density changes of valence electrons are neglected. Consequently, the integrated diffuse intensities remain unchanged if the average structure is not altered by the degree of order. The latter condition is obeyed in cases where a geometrical long-range order of the lattice is independent of the degree of order, and no long-range order in the structure exists. This law is extremely useful for the interpretation of diffuse scattering. Unfortunately, intensity integration over coinciding sharp and diffuse maxima does not necessarily lead to a structure determination of the corresponding undistorted structure. This integration may be useful for antiphase domains without major structural changes at the boundaries. In all other cases the deviations of domains (or clusters) from the averaged structure determine the intensities of maxima which are no longer correlated with those of the average structure.

If the integrated intensity of diffuse scattering is comparable with, or even larger than, those of the Bragg peaks it is useful to begin the interpretation with a careful statistical study of the diffuse intensities. Intensity statistics can be applied in a way similar to the intensity statistics in classical structure determination. The following rules are briefly discussed in order to enable a semi-quantitative interpretation of the essential features of disorder to be realized.

(1) First, it is recommended that the integrated intensities be studied in certain areas of reciprocal space.

(2) Since low-angle scattering is very sensitive to fluctuations of densities, the most important information can be drawn from its intensity behaviour. If there is at least a one-dimensional sublattice in reciprocal space without diffuse scattering, it may often be concluded that there is no important low-angle scattering either. This law is subject to the condition of a sufficient number of reflections obeying this extinction rule without any exception.

(3) If the diffuse scattering shows maxima and minima, it should be checked whether the maxima observed may be approximately assigned to a lattice in reciprocal space. Obviously, this condition can hardly be met exactly if these maxima are modulated by a kind of structure factor, which causes displacements of maxima proportional to the gradient of this structure factor. Hence this

influence may well be estimated from a careful study of the complete diffuse diffraction pattern.

It should then be checked whether the corresponding lattice represents a sub- or a superlattice of the structure. An increase of the width of reflections as a function of growing $|\mathbf{H}|$ indicates strained clusters of sub- or superlattice.

(4) The next step is the search for extinction rules of diffuse scattering. The simplest is the lack of low-angle scattering which has already been mentioned above. Since diffuse scattering is generally given by equation (4.2.2.13)

$$\begin{aligned} I_d(\mathbf{H}) &= \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \\ &= \sum_{\mu} p_{\mu} |F_{\mu}(\mathbf{H})|^2 - \left| \sum_{\mu} p_{\mu} F_{\mu}(\mathbf{H}) \right|^2, \end{aligned}$$

it may be concluded that this condition is fulfilled in cases where all structural elements participating in disorder differ by translations only (stacking faults, antiphase domains *etc.*). They add phase factors to the various structure factors, which may become $n2\pi$ ($n = \text{integer}$) for specific values of the reciprocal vector \mathbf{H} . If all p_{μ} are equivalent by symmetry:

$$p \sum_{\mu} |F_{\mu}(\mathbf{H})|^2 - [p \sum_{\mu} F_{\mu}(\mathbf{H})][p \sum_{\mu} F_{\mu}^+(\mathbf{H})] = 0.$$

Other possibilities of vanishing diffuse scattering may be derived in a similar manner for special reflections if glide operations are responsible for disorder. Since we are concerned with disordered structures, these glide operations need not necessarily be a symmetry operation of the lattice. It should be pointed out, however, that all these extinction rules of diffuse scattering are a kind of 'anti'-extinction rule, because they are valid for reflections having maximum intensity for the sharp reflections unless the structure factor itself vanishes.

(5) Furthermore, it is important to plot the integrated intensities of sharp and diffuse scattering as a function of the reciprocal coordinates at least in a semi-quantitative way. If the ratio of integrated intensities remains constant in the statistical sense, we are predominantly concerned with a density phenomenon. It should be pointed out, however, that a particle-size effect of domains behaves like a density phenomenon (density changes at the boundary!).

If the ratio of 'diffuse' to 'sharp' intensities increases with diffraction angle, we have to take into account atomic displacements. A careful study of this ratio yields very important information on the number of displaced atoms. The result has to be discussed separately for domain structures if the displacements are equal in the subcells of a single domain, but different for the various domains. In the case of two domains with displacements of all atoms the integrated intensities of sharp and diffuse reflections become statistically equal for large $|\mathbf{H}|$. Other rules may be derived from statistical considerations.

(6) The next step of a semi-quantitative interpretation is the check of the intensity distribution of diffuse reflections in reciprocal space. Generally this modulation is simpler than that of the sharp reflections. Hence it is frequently possible to start a structure determination with diffuse scattering. This method is extremely helpful for one- and two-dimensional disorder where partial structure determinations yield valuable information, even for the evaluation of the average structure.

(7) In cases where no sub- or superlattice belonging to diffuse scattering can be determined, a careful check of integrated intensities in the surroundings of Bragg peaks should again be performed. If systematic absences are found, the disorder is most probably restricted to specific lattice sites which may also be found in the average structure. The accuracy, however, is much lower here. If no such effects correlated with the average structure are

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observed, the disorder problem is related to a distribution of molecules or clusters with a structure differing from the average structure. As pointed out in Section 4.2.3.1 the problem of the representative structure(s) of the molecule(s) or the cluster(s) should be solved. Furthermore their distribution function(s) is (are) needed. In this particular case it is very useful to start with a study of diffuse intensity at low diffraction angles in order to acquire the information about density effects. Despite the contribution to sharp reflections, one should remember that the information derived from the average structure may be very low (e.g. small displacements, low concentrations *etc.*).

(8) As pointed out above, a Patterson picture – or strictly speaking a difference Patterson ($|\Delta F|^2$ -Fourier synthesis) – may be very useful in this case. This method is promising in the case of disorder in molecular structures where the molecules concerned are at least partly known. Hence the interpretation of the difference Patterson may start with some internal molecular distances. Non-molecular structures show some distances of the average structure. Consequently a study of the important distances will yield information on displacements or replacements in the average structure. For a detailed study of this matter the reader is referred to the literature (Schwartz & Cohen, 1977).

Although it is highly improbable that exactly the same diffraction picture will really be found, the use of an atlas of optical transforms (Wooster, 1962; Harburn *et al.*, 1975; Welberry & Withers, 1987) may be very helpful at the beginning of any study of diffuse scattering. The most important step is the separation of the distribution function from the molecular scattering. Since this information may be derived from a careful comparison of low-angle diffraction with the remaining sharp reflections, this task is not too difficult. If the influence of the distribution function is unknown, the reader is strongly advised to disregard the immediate neighbourhood of Bragg peaks in the first step of the interpretation. Obviously information may be lost in this way but, as has been shown in the past, much confusion caused by the attempt to interpret the scattering near the Bragg peaks with specific structural properties of a cluster or molecular model is avoided. The inclusion of this part of diffuse scattering can be made after the complete interpretation of the change of the influence of the distribution function on diffraction in the far-angle region.

4.2.4. Quantitative interpretation

4.2.4.1. Introduction

In these sections quantitative interpretations of the elastic part of diffuse scattering (X-rays and neutrons) are outlined. Although similar relations are valid, magnetic scattering of neutrons is excluded. Obviously, all disorder phenomena are strongly temperature dependent if thermal equilibrium is reached. Consequently, the interpretation of diffuse scattering should include a statistical thermodynamical treatment. Unfortunately, no quantitative theory for the interpretation of structural phenomena is so far available: all quantitative solutions introduce formal order parameters such as correlation functions or distributions of defects. At low temperatures (low concentration of defects) the distribution function plays the dominant role in diffuse scattering. With increasing temperature the number of defects increases with corresponding strong interactions between them. Therefore, correlations become increasingly important, and phase transformations of first or higher order may occur which need a separate theoretical treatment. In many cases large fluctuations of structural properties occur which are closely related to the dynamical properties of the crystal. Theoretical approximations are possible

but their presentation is far beyond the scope of this article. Hence we restrict ourselves to formal parameters in the following.

Point defects or limited structural units, such as molecules, clusters of finite size *etc.*, may only be observed in diffraction for a sufficiently large number of defects. This statement is no longer true in high-resolution electron diffraction where single defects may be observed either by diffraction or by optical imaging if their contrast is high enough. Hence, electron microscopy and diffraction provide valuable methods for the interpretation of disorder phenomena.

The arrangement of a finite assembly of structural defects is described by its structure and its three-dimensional (3D) distribution function. Structures with a strict 1D periodicity (chain-like structures) need a 2D distribution function, while for structures with a 2D periodicity (layers) a 1D distribution function is sufficient. Since the distribution function is the dominant factor in statistics with correlations between defects, we define the dimensionality of disorder as that of the corresponding distribution function. This definition is more effective in diffraction problems because the dimension of the disorder problem determines the dimension of the diffuse scattering: 1D diffuse streaks, 2D diffuse layers, or a general 3D diffuse scattering.

Strictly speaking, completely random distributions cannot be realized as shown in Section 4.2.3. They occur approximately if the following conditions are satisfied.

(1) The average volume of all defects including their surrounding strain fields NcV_d (N = number of unit cells, c = concentration of defects, V_d = volume of the defect with $V_d > V_c$, V_c = volume of the unit cell) is small in comparison with the total volume NV_c of the crystal, or $V_c \gg cV_d$.

(2) Interactions between the defects are negligible. These conditions, however, are valid in very rare cases only, *i.e.* where small concentrations and vanishing strain fields are present. Remarkable exceptions from this rule are real point defects without interactions, such as isotope distribution (neutron diffraction!), or the system AuAg at high temperature.

As already mentioned, disorder phenomena may be observed in thermal equilibrium. Two completely different cases have to be considered.

(1) The concentration of defects is given by the chemical composition, *i.e.* impurities in a closed system.

(2) The number of defects increases with temperature and also depends on pressure or other parameters, *i.e.* interstitials, voids, static displacements of atoms, stacking faults, dislocations *etc.*

In many cases the defects do not occur in thermal equilibrium. Nevertheless, their diffuse scattering is temperature dependent because of the anomalous thermal movements at the boundary of the defect. Hence, the observation of a temperature-dependent behaviour of diffuse scattering cannot be taken as a definite criterion of thermal equilibrium without further careful interpretation.

Ordering of defects may take place in a very anisotropic manner. This is demonstrated by the huge number of examples of 1D disorder. As shown by Jagodzinski (1963) this type of disorder cannot occur in thermal equilibrium for the infinite crystal. This type of disorder is generally formed during crystal growth or mechanical deformation. Similar arguments may be applied to 2D disorder. This is a further reason why the so-called Ising model can hardly be used in order to obtain interaction energies of structural defects. From these remarks it becomes clear that order parameters are more or less formal parameters without strict thermodynamical meaning.

The following section is organized as follows: first we discuss the simple case of 1D disorder where reliable solutions of the diffraction problem are available. Intensity calculations of diffuse scattering of 2D disorder by chain-like structures follow. Finally, the 3D case is treated, where formal solutions of the diffraction

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problem have been tried and applied successfully to metallic systems to some extent. A short concluding section concerns the special phenomenon of orientational disorder.

4.2.4.2. One-dimensional disorder of ordered layers

As has been pointed out above, it is often useful to start the interpretation of diffuse scattering by checking the diffraction pattern with respect to the dimensionality of the disorder concerned. Since each disordered direction in the crystal demands a violation of the corresponding Laue condition, this question may easily be answered by looking at the diffuse scattering. Diffuse streaks in reciprocal space are due to a one-dimensional violation of the Laue conditions, and will be called one-dimensional disorder. This kind of order is typical for layer structures, but it is frequently observed in cases where several sequences of layers do not differ in the interactions of next-nearest neighbours. Typical examples are structures which may be described in terms of close packing, *e.g.* hexagonal and cubic close packing.

For a quantitative interpretation of diffuse streaks we need one-dimensional correlation functions, which may uniquely be determined if a single independent correlation function is active. According to equation (4.2.3.28) Fourier transformation yields the information required. In all other cases a specific model has to be suggested for a full interpretation of diffuse streaks. Another comment seems to be necessary: disorder parameters can be defined uniquely only if the diffraction pattern allows for a differentiation between long-range and short-range order. This question can at least partly be answered by studying the line width of sharp reflections with a very good resolution. Since integrated intensities of sharp reflections have to be separated from the diffuse scattering, this question is of outstanding importance in most cases. Inclusion of diffuse parts in the diffraction pattern during intensity integration of sharp reflections may lead to serious errors in the interpretation of the average structure.

The existence of diffuse streaks in more than one direction of reciprocal space means that the diffraction problem is no longer one-dimensional. Sometimes the problem may be treated independently, if the streaks are sharp, and no interference effects may be observed in the diffraction pattern in areas where the diffuse streaks do overlap. In all other cases there are correlations between the various directions of one-dimensional disorder which may be determined with the aid of a model covering more than one of the pertinent directions of disorder.

Before starting the discussion of the quantitative solution of the one-dimensional problem, some remarks should be made on the usefulness of quantitative disorder parameters. It is well known from statistical thermodynamics that a one-dimensional system cannot show long-range order above $T = 0$ K. Obviously, this statement is in contradiction with many experimental observations where long-range order is realized even in layer structures. The reason for this behaviour is given by the following arguments which are valid for any structure. Let us assume a structure with strong interactions at least in two directions. From the theoretical treatment of the two-dimensional Ising model it is known that such a system shows long-range order below a critical temperature T_c . This statement is true even if the layer is finite, although the strict thermodynamic behaviour is not really critical in the thermodynamical sense. A three-dimensional crystal can be constructed by adding layer after layer. Since each layer has a typical two-dimensional free energy, the full statistics of the three-dimensional crystal may be calculated by introducing a specific free energy for the various stackings of layers. Obviously, this additional energy has to include terms describing potential and entropic energies as well. They may be formally developed into contributions of next, overnext *etc.* nearest neighbours. Apparently, the contribution to

entropy must include configurational and vibrational parts which are strongly coupled. As long as the layers are finite, there is a finite probability of a fault in the stacking sequence of layers which approaches zero with increasing extension of the layers. Consequently, the free energy of a change in the favourite stacking sequence becomes infinite quadratically with the size of the layer. Therefore, the crystal should be either completely ordered or disordered; the latter case can only be realized if the free energies of one or more stacking sequences are exactly equal (very rare, but possible over a small temperature range of phase transformations). An additional positive entropy associated with a deviation from the periodic stacking sequence may lead to a kind of competition between entropy and potential energy, in such a way that periodic sequences of faults result. Obviously, this situation occurs in the transition range of two structures differing only in their stacking sequence. On the other hand, one must assume that defects in the stacking sequence may be realized if the size of the layers is small. This situation occurs during crystal growth, but one should remember that the number of stacking defects should decrease with increasing size of the growing crystal. Apparently, this rearrangement of layers may be suppressed as a consequence of relaxation effects. The growth process itself may influence the propagation of stacking defects and, consequently, the determination of stacking-fault probabilities, aiming at an interpretation of the chemical bonding seems to be irrelevant in most cases.

The quantitative solution of the diffraction problem of one-dimensional disorder follows a method similar to the Ising model. As long as next-nearest neighbours alone are considered, the solution is very simple only if two possibilities of structure factors are to be taken into account. Introducing the probability of equal pairs 1 and 2, α , one arrives at the known solution for the *a priori* probability p_μ and *a posteriori* probabilities $p_{\mu\nu}(\mathbf{m})$, respectively. In the one-dimensional Ising model with two spins and the interaction energies $(U \mp \Delta U)/k_B T$, defining the pair probability $[\alpha = p_{11}(\mathbf{1})]$

$$\alpha = \frac{\exp\{\pm \Delta U/k_B T\}}{[\exp\{+\Delta U/k_B T\} + \exp\{-\Delta U/k_B T\}]}$$

the full symmetry is $p_1 = p_2 = \frac{1}{2}$, and $p_{11}(\mathbf{m}) = p_{22}(\mathbf{m})$.

Consequently:

$$p_{12}(\mathbf{m}) = p_{22}(\mathbf{m}) = 1 - p_{11}(\mathbf{m}).$$

The scattered intensity is given by

$$I(\mathbf{H}) = L(h, k) \sum_{\mathbf{m}} \langle FF_m^+ \rangle (N - |m|) \exp\{-2\pi i m l\}, \quad (4.2.4.1)$$

where $\mathbf{m} = m\mathbf{c}$, N = number of unit cells in the \mathbf{c} direction and $\langle FF_m^+ \rangle$ depends on λ_1, λ_2 which are the eigenvalues of the matrix

$$\begin{pmatrix} \alpha & 1 - \alpha \\ 1 - \alpha & \alpha \end{pmatrix}.$$

From the characteristic equation

$$\lambda^2 - 2\alpha\lambda - 1 + 2\alpha = 0 \quad (4.2.4.2)$$

one has

$$\lambda_1 = 1; \quad \lambda_2 = 2\alpha - 1. \quad (4.2.4.2a)$$

λ_1 describes a sharp Bragg reflection (average structure) which need not be calculated. Its intensity is simply proportional to $\langle F(\mathbf{H}) \rangle$. The second characteristic value yields a diffuse reflection in the same position if the sign is positive ($\alpha > 0.5$), and in a position displaced by $\frac{1}{2}$ in reciprocal space if the sign is negative ($\alpha < 0.5$). Because of the symmetry conditions $p_{11}(\mathbf{m})$ only is needed; it may be determined with the aid of the boundary conditions

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$$p_{11}(\mathbf{0}) = 1, \quad p_{11}(\mathbf{1}) = \alpha,$$

and the general relation that $p_{\mu\mu'}(\mathbf{m})$ is given by

$$p_{\mu\mu'}(\mathbf{m}) = c'_{\mu\mu'}\lambda_1^m + c''_{\mu\mu'}\lambda_2^m.$$

The final solution of our problem yields simply:

$$p_{11}(\mathbf{m}) = \frac{1}{2} + \frac{1}{2}\lambda_2^m = p_{22}(\mathbf{m}),$$

$$p_{12}(\mathbf{m}) = \frac{1}{2} - \frac{1}{2}\lambda_2^m = p_{21}(\mathbf{m}).$$

The calculation of the scattered intensity is now performed with the general formula

$$I(\mathbf{H}) = L(h, k) \sum_m \sum_{\mu, \mu'} p_{\mu\mu'}(\mathbf{m}) F_{\mu} F_{\mu'}^+ (N - |m|) \times \exp\{-2\pi i m l\}. \quad (4.2.4.3)$$

Evaluation of this expression yields

$$I(\mathbf{H}) = L(h, k) \sum_m (N - |m|) \exp\{-2\pi i m l\} \times [|\frac{1}{2}(F_1 + F_2)|^2 \lambda_1^m + |\frac{1}{2}(F_1 - F_2)|^2 \lambda_2^m]. \quad (4.2.4.4)$$

Since the characteristic solutions of the problem are real:

$$I(\mathbf{H}) = L(\mathbf{h}) |(F_1 + F_2)/2|^2 + L(h, k) |(F_1 - F_2)/2|^2 \times \frac{1 - |\lambda_2|^2}{1 - 2\lambda_2 \cos 2\pi l + |\lambda_2|^2}. \quad (4.2.4.5)$$

This particle size effect has been neglected in (4.2.4.5). This result confirms the fact mentioned above that the sharp Bragg peaks are determined by the averaged structure factor and the diffuse one by its mean-square deviation.

For the following reason there are no examples for quantitative applications: two different structures generally have different lattice constants; hence the original assumption of an undisturbed lattice geometry is no longer valid. The only case known to the authors is the typical lamellar structure of plagioclases, reported by Jagodzinski & Korekawa (1965). The authors interpret the well known 'Schiller effect' as a consequence of optical diffraction. Hence, the size of the lamellae is of the order of 2000 Å. This long-period superstructure cannot be explained in terms of next-nearest-neighbour interactions. In principle, however, the diffraction effects are similar: instead of the diffuse peak as described by the second term in equation (4.2.4.5), satellites of first and second order, *etc.* accompanying the Bragg peaks are observed. The study of this phenomenon (Korekawa & Jagodzinski, 1967) has not so far resulted in a quantitative interpretation.

Obviously, the symmetry relation used in the formulae discussed above is only valid if the structures described by the F_{μ} are related by symmetries such as translations, rotations or combinations of both. The type of symmetry has an important influence on the diffraction pattern.

(1) Translation parallel to the ordered layers

If the translation vector between the two layers in question is such that $2\Delta\mathbf{r}$ is a translation vector parallel to the layer, there are two relevant structure factors

$$F_1, F_2 = F_1 \exp(2\pi i \mathbf{H} \cdot \Delta\mathbf{r}).$$

$\mathbf{H} \cdot \Delta\mathbf{r}$ may be either an integer or an integer + $\frac{1}{2}$. Since any integer may be neglected because of the translation symmetry parallel to the layer, we have $F_1 = F_2$ in the former case, and $F_1 = -F_2$ in the latter. As a consequence either the sharp reflections given in equation (4.2.4.4) vanish, or the same is true for the diffuse ones.

Hence, the reciprocal lattice may be described in terms of two kinds of lattice rows, sharp and diffuse, parallel to the reciprocal coordinate l .

Disorder of this type is observed very frequently. One of the first examples was wollastonite, CaSiO_3 , published by Jefferey (1953). Here the reflections with $k = 2n$ are sharp Bragg peaks without any diffuse scattering. Diffuse streaks parallel to $(h00)$, however, are detected for $k = 2n + 1$. In the light of the preceding discussion, the translation vector is $\frac{1}{2}\mathbf{b}$, and the plane of ordered direction (plane of intergrowth of the two domains) is (100) . Hence the displacement is parallel to the said plane. Since the intensity of the diffuse lines does not vary according to the structure factor involved, the disorder cannot be random. The maxima observed are approximately in the position of a superstructure, generated by large domains without faults in the stacking sequence, mutually displaced by $\frac{1}{2}\mathbf{b}$ (antiphase domains). This complicated ordering behaviour is typical for 1D order and may easily be explained by the above-mentioned fact that an infinitely extended interface between two domains causes an infinite unfavourable energy (Jagodzinski, 1964b, p. 188). Hence, a growing crystal should become increasingly ordered. This consideration explains why the agreement between a 1D disorder theory and experiment is often so poor.

Examples where more than one single displacement vector occur are common. If these are symmetrically equivalent all symmetries have to be considered. The most important cases of displacements differing only by translation are the well known close-packed structures (see below). A very instructive example is the mineral maucherite (approximately Ni_4As_3). According to Jagodzinski & Laves (1947) the structure has the following disorder parameters: interface (001) , displacement vectors $[000]$, $[\frac{1}{2}00]$, $[0\frac{1}{2}0]$, $[\frac{1}{2}\frac{1}{2}0]$. From equation (4.2.4.5) we obtain:

$$\langle F(\mathbf{H}) \rangle = [1 + \exp\{\pi i h\} + \exp\{\pi i k\} + \exp\{\pi i(h+k)\}]/4.$$

Hence there are sharp reflections for $h, k = \text{even}$, and diffuse ones otherwise. Further conclusions may be drawn from the average structure.

(2) Translation perpendicular to the ordered layers

If the translation is $\mathbf{c}/2$ the structure factors are:

$$F_2 = F_1 \exp\{2\pi i l\}$$

$$F_1 = F_2 \text{ for } l = \text{even}$$

$$F_1 = -F_2 \text{ for } l = \text{odd}.$$

There are sharp ($l = 2n$) and diffuse ($l = 2n + 1$) reflections on all reciprocal-lattice rows discussed above.

Since the sharp and diffuse reflections occur on the same reciprocal line there is a completely different behaviour compared with the preceding case. In general, a component of any displacement vector perpendicular to the interface gives rise to a change in chemical composition as shown in the next example: in a binary system consisting of A and B atoms with a tendency towards an alternating arrangement of A and B layers, any fault in the sequence $BABAB|BABAB|B$ increases the number of B atoms (or A atoms). Generally such kinds of defects will lead to an interface with a different lattice constant, at least in the direction perpendicular to the interface. Consequently the exact displacement vectors of $\frac{1}{2}, \frac{1}{3}, \frac{1}{4}$ are rare. Since ordered structures should be realized in the 1D case, incommensurate superstructures will occur which are very abundant during ordering processes. An interesting example has been reported and interpreted by Cowley (1976) where the displacement vector has a translational period of $\frac{1}{4}$ perpendicular to the plane of intergrowth. Reflections $00l$ and $22l$ with $l = 4n$ are sharp, all remaining reflections more or less diffuse. Since the maxima $(111), (133)$ show a systematically different

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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 \mathbf{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 \mathbf{m} . The calculation of characteristic values yields

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

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

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

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

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

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 $\mathbf{h} \cdot \mathbf{r} = \text{integer}$, where \mathbf{r} is parallel to the layer, more than two structure factors have to be taken into account. If $n\mathbf{h} \cdot \mathbf{r} = \text{integer}$, 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 \mathbf{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

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

Equation (4.2.4.8) gives sharp Bragg reflections for $\mathbf{H} \cdot \mathbf{r} / n = \text{integer}$; 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 $\text{TiO}_2\text{-SnO}_2$. 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:

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

hence

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

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:

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

For the case of close packing of spheres and some other problems any configuration of \mathbf{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:

$$\begin{aligned} &123, 231, 312; \quad 132, 213, 321; \\ &121, 232, 313; \quad 131, 212, 323. \end{aligned}$$

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.

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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

	$F_{\mu'}^+$	(1)	(2)	(3)	(4)
F_μ		312, 123(ε^+), 231(ε)	212, 323(ε^+), 131(ε)	213, 321(ε^+), 132(ε)	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 $h - k = 0 \pmod{3}$, $\varepsilon = +1$, there are two quadratic equations:

$$\begin{aligned} \lambda^2 - (\alpha_1 + \alpha_2)\lambda - 1 + \alpha_1 + \alpha_2 &= 0 \\ \lambda^2 - (\alpha_1 - \alpha_2)\lambda + 1 - \alpha_1 - \alpha_2 &= 0 \end{aligned} \quad (4.2.4.9)$$

with solutions

$$\begin{aligned} \lambda_1 &= 1, & \lambda_2 &= \alpha_1 + \alpha_2 - 1 \\ \lambda_{3/4} &= \frac{\alpha_1 - \alpha_2}{2} \pm \left[\frac{(\alpha_1 - \alpha_2)^2}{4} - 1 + \alpha_1 - \alpha_2 \right]^{1/2}. \end{aligned} \quad (4.2.4.10)$$

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

reflections for $l = \text{integer}$, and diffuse ones in a position determined by the sequence probabilities α_1 and α_2 (position either $l = \text{integer}$, $l = \frac{1}{2} + \text{integer}$, 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 $k - k = 0 \pmod{3}$ 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 $(h - k) \equiv 0 \pmod{3}$ become diffuse if $l \neq 0$, and the diffuseness increases with l . A similar behaviour results for the remaining reciprocal-lattice rows.

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

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

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

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

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

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

4.2.4.3. Two-dimensional disorder of chains

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

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

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

4.2.4.3.1. Scattering by randomly distributed collinear chains

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

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

is described by one of the Laue equations:

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

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

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

where ξ denotes the correlation length.

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

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

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

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

The Patterson function is:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Along the theory of Fourier series one has:

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

or with:

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

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

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

Analogously, one has

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

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

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

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

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

Special cases are:

(a) *Complete cylinder symmetry*

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

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

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

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

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

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

(c) *Vertical mirror planes*

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

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

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

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

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

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

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

one has:

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

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

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

or

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

Intensity in the l th diffuse layer is given by

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

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

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

or

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

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

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

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

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

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

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

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

4.2.4.3.2. Disorder within randomly distributed collinear chains

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

4.2.4.3.2.1. General treatment

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

replaced by a distribution:

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

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

The Patterson function is given by

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

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

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

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

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

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

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

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

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

with

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

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

4.2.4.3.2.2. Orientational disorder

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

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

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

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

where

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

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

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4.2.4.3.2.3. Longitudinal disorder

In this context the structure factor of a chain molecule is neglected. Irregular distances between the molecules within a chain occur owing to the shape of the molecules, intrachain interactions and/or interaction forces *via* a surrounding matrix. A general discussion is given by Guinier (1963). It is convenient to reformulate the discrete Patterson function, *i.e.* the correlation function (4.2.4.39).

$$w(z) = N\delta(z) + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+1})] + \sum_{\nu} \delta[z \pm (z_{\nu} - z_{\nu+2})] + \dots \quad (4.2.4.39a)$$

in terms of continuous functions $a_{\mu}(z)$ which describe the probability of finding the μ th neighbour within an arbitrary distance

$$w'(z) = w(z)/N = \delta(z) + a_1(z) + a_{-1}(z) + \dots + a_{\mu}(z)a_{-\mu}(z) + \dots \quad (4.2.4.45)$$

$$[\int a_{\mu}(z) dz = 1, a_{\mu}(z) = a_{-\mu}(-z)].$$

There are two principal ways to define $a_{\mu}(z)$. The first is the case of a well defined one-dimensional lattice with positional fluctuations of the molecules around the lattice points, *i.e.* long-range order is retained: $a_{\mu}(z) = \mu c_0 + z_{\mu}$, where z_{μ} denotes the displacement of the μ th molecule in the chain. Frequently used are Gaussian distributions:

$$c' \exp\{-(z - \mu c_0)^2/2\Delta^2\}$$

(c' = normalizing constant; Δ = standard deviation). Fourier transformation [equation (4.2.4.45)] gives the well known result

$$I_d \sim (1 - \exp\{-L^2\Delta^2\}),$$

i.e. a monotonically increasing intensity with L (modulation due to a molecular structure factor neglected). This result is quite analogous to the treatment of the scattering of independently vibrating atoms. If (short-range) correlations exist between the molecules the Gaussian distribution is replaced by a multivariate normal distribution where correlation coefficients κ^{μ} ($0 < \kappa < 1$) between a molecule and its μ th neighbour are incorporated. κ^{μ} is defined by the second moment: $\langle z_0 z_{\mu} \rangle / \Delta^2$.

$$a_{\mu}(z) = c'' \exp\{-(z - \mu c_0)^2/2\Delta^2(1 - \kappa^{\mu})\}.$$

Obviously the variance increases if the correlation diminishes and reaches an upper bound of twice the single site variance. Fourier transformation gives an expression for diffuse intensity (Welberry, 1985):

$$I_d(L) \sim \exp\{-L^2\Delta^2\} \sum_j (-L^2\Delta^2)^j / j! \times (1 - \kappa^{2j}) / (1 + \kappa^{2j} - 2\kappa^j \cos 2\pi L c_0). \quad (4.2.4.46)$$

For small Δ , terms with $j > 1$ are mostly neglected. The terms become increasingly important with higher values of L . On the other hand, κ^j becomes smaller with increasing j , each additional term in equation (4.2.4.46) becomes broader and, as a consequence, the diffuse planes in reciprocal space become broader with higher L .

In a different way – in the paracrystal method – the position of the second and subsequent molecules with respect to some reference zero point depends on the *actual* position of the predecessor. The variance of the position of the μ th molecule relative to the first becomes unlimited. There is a continuous transition to a fluid-like behaviour of the chain molecules. This 1D paracrystal (sometimes called distortions of second kind) is only a special case of the 3D paracrystal concept (see Hosemann & Bagchi, 1962; Wilke, 1983). Despite some difficulties with this

concept (Brämer, 1975; Brämer & Ruland, 1976) it is widely used as a theoretical model for describing diffraction of highly distorted lattices. One essential development is to limit the size of a paracrystalline grain so that fluctuations never become too large (Hosemann, 1975).

If this concept is used for the 1D case, $a_{\mu}(z)$ is defined by convolution products of $a_1(z)$. For example, the probability of finding the next-nearest molecule is given by

$$a_2(z) = \int a_1(z') a_1(z - z') dz' = a_1(z) * a_1(z)$$

and, generally:

$$a_{\mu}(z) = a_1(z) * a_1(z) * a_1(z) * \dots * a_1(z)$$

(μ -fold convolution).

The mean distance between next-nearest neighbours is

$$\langle c \rangle = \int z' a_1(z') dz'$$

and between neighbours of the μ th order: $\mu \langle c \rangle$. The average value of $a_{\mu} = 1/\langle c \rangle$, which is also the value of $w(z)$ for $z > z_k$, where the distribution function is completely smeared out. The general expression for the interference function $G(L)$ is

$$G(L) = 1 + \sum_{\mu} \{F^{\mu} + F^{+\mu}\} = \text{Re}\{(1 + F)/(1 - F)\} \quad (4.2.4.47)$$

with $F(L) \leftrightarrow a_1(z)$, $F^{\mu}(L) \leftrightarrow a_{\mu}(z)$.

With $F = |F|e^{i\chi}$ ($\chi = L\langle c \rangle$), equation (4.2.4.47) is written:

$$G(L) = [1 - |F(L)|^2] / [1 - 2|F(L)| \cos \chi + |F(L)|^2]. \quad (4.2.4.47a)$$

[Note the close similarity to the diffuse part of equation (4.2.4.5), which is valid for 1D disorder problems.]

This function has maxima of height $(1 + |F|)/(1 - |F|)$ and minima of height $(1 - |F|)/(1 + |F|)$ at positions lc^* and $(l + \frac{1}{2})c^*$, respectively. With decreasing $|F|$ the oscillations vanish; a critical L value (corresponding to z_k) may be defined by $G_{\max}/G_{\min} \lesssim 1.2$. Actual values depend strongly on $F(\mathbf{H})$.

The paracrystal method is substantiated by the choice $a_1(z)$, *i.e.* the disorder model. Again, frequently used is a Gaussian distribution:

$$a_1(z) = 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \langle c \rangle)^2/2\Delta^2\}$$

$$a_{\mu}(z) = 1/\sqrt{\mu} \cdot 1/\sqrt{2\pi}\Delta \cdot \exp\{-(z - \mu\langle c \rangle)^2/2\mu\Delta^2\}$$

$$(4.2.4.48)$$

with the two parameters $\langle c \rangle$, Δ .

There are peaks of height $1/[\pi^2 L^2 (\Delta/\langle c \rangle)^2]$ which obviously decrease with L^2 and $(\Delta/\langle c \rangle)^2$. The oscillations vanish for $|F| \simeq 0.1$, *i.e.* $1/\langle c \rangle \simeq 0.25/\Delta$. The width of the m th peak is $\Delta_m = \sqrt{m}\Delta$. The integral reflectivity is approximately $1/\langle c \rangle [1 - \pi^2 L^2 (\Delta/\langle c \rangle)^2]$ and the integral width (defined by integral reflectivity divided by peak reflectivity) (background subtracted!) $1/\langle c \rangle \pi^2 L^2 (\Delta/\langle c \rangle)^2$ which, therefore, increases with L^2 . In principle the same results are given by Zernike & Prins (1927). In practice a single Gaussian distribution is not fully adequate and modified functions must be used (Rosshirt *et al.*, 1985).

A final remark concerns the normalization [equation (4.2.4.39)]. Going from (4.2.4.39) to (4.2.4.45) it is assumed that N is a large number so that the correct normalization factors $(N - |\mu|)$ for each $a_{\mu}(z)$ may be approximated by a uniform N . If this is not true then

$$G(L) = N + \sum_{\mu} (N - |\mu|) (F^{\mu} + F^{+\mu}) = N \text{Re} \{(1 + |F|)/(1 - |F|)\} - 2 \text{Re} \{|F|(1 - |F|^N)/(1 - |F|^2)\}. \quad (4.2.4.49)$$

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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 \mathbf{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 $\text{Hg}_{3-6}\text{AsF}_6$ (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 \mathbf{a} and/or \mathbf{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

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

(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:

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

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 \mathbf{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 \mathbf{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 \mathbf{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 \mathbf{a}^* (and/or \mathbf{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

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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 understanding 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

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

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 ν th 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

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

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

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

$\pi_\nu(\mathbf{r})$ consists of $\alpha_\nu N$ points, where $N = N_1 N_2 N_3$ is the total (large) number of unit cells and α_ν denotes the *a priori* probability (concentration) of the ν th cell occupation.

It is now useful to introduce

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

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):

$$\begin{aligned} \sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r}) \sum_\nu \alpha_\nu F_\nu(\mathbf{r}) \\ &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) + l(\mathbf{r}) \langle F(\mathbf{r}) \rangle. \end{aligned} \quad (4.2.4.59)$$

Similarly:

$$\Delta F_\nu(\mathbf{r}) = F_\nu(\mathbf{r}) - \langle F(\mathbf{r}) \rangle \quad (4.2.4.60)$$

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

Using (4.2.4.60) it follows from (4.2.4.58) that

$$\begin{aligned} \sum_\nu \pi_\nu(\mathbf{r}) * F_\nu(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) \\ &\quad + \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \langle F(\mathbf{r}) \rangle + l(\mathbf{r}) * \langle F(\mathbf{r}) \rangle \\ &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) + l(\mathbf{r}) * \langle F(\mathbf{r}) \rangle. \end{aligned} \quad (4.2.4.61)$$

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

$$\begin{aligned} I(\mathbf{H}) &= \left| \sum_\nu \Delta\Pi_\nu(\mathbf{H}) \Delta F_\nu(\mathbf{H}) \right|^2 + |L(\mathbf{H}) \langle F(\mathbf{H}) \rangle|^2 \\ &\quad + L(\mathbf{H}) \left\{ \langle F^+(\mathbf{H}) \rangle \sum_\nu \Delta\Pi_\nu(\mathbf{H}) F_\nu(\mathbf{H}) \right. \\ &\quad \left. + \langle F^+(\mathbf{H}) \rangle \sum_\nu \Delta\Pi_\nu^+(\mathbf{H}) F_\nu^+(\mathbf{H}) \right\}. \end{aligned} \quad (4.2.4.62)$$

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

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

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

$$\begin{aligned} i_d(\mathbf{r}) &= \sum_\nu \Delta\pi_\nu(\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \sum_{\nu'} \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) \\ &= \sum_\nu \sum_{\nu'} \Delta\pi_\nu(\mathbf{r}) * \Delta\pi_{\nu'}(-\mathbf{r}) * \Delta F_\nu(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) \end{aligned} \quad (4.2.4.64)$$

and with (4.2.4.58):

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$$i_d(\mathbf{r}) = \sum_{\nu} \sum_{\nu'} [\pi_{\nu}(\mathbf{r}) - \alpha_{\nu} l(\mathbf{r})] * [\pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \quad (4.2.4.65)$$

Evaluation of this equation for a single term yields

$$[\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu} l(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - \alpha_{\nu'} l(\mathbf{r}) * \pi_{\nu}(\mathbf{r}) + \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) * l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(\mathbf{r}). \quad (4.2.4.66)$$

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

$$[\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r}) + N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) = [\pi_{\nu}(\mathbf{r}) * \pi_{\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}). \quad (4.2.4.67)$$

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:

$$[Nl(\mathbf{r})\alpha_{\nu}p_{\nu\nu'}(-\mathbf{r}) - N \alpha_{\nu} \alpha_{\nu'} l(\mathbf{r})] * \Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r}) = N \alpha_{\nu} [\alpha_{\nu'} p_{\nu\nu'}(-\mathbf{r}) l(\mathbf{r})] * [\Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \quad (4.2.4.68)$$

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:

$$\sum_{\nu} \alpha_{\nu} = 1 \quad (4.2.4.69a)$$

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

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

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

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

$$i_d(\mathbf{r}) = N \sum_{\nu} \sum_{\nu'} [\alpha_{\nu} p'_{\nu\nu'}(-\mathbf{r}) l(\mathbf{r})] * [\Delta F_{\nu}(\mathbf{r}) * \Delta F_{\nu'}(-\mathbf{r})] \quad (4.2.4.70)$$

and Fourier transformation yields

$$I_d(\mathbf{H}) = N \sum_{\nu} \sum_{\nu'} [\alpha_{\nu} P'_{\nu\nu'}(-\mathbf{H}) * L(\mathbf{H})] \Delta F_{\nu}(\mathbf{H}) \Delta F_{\nu'}^+(\mathbf{H}). \quad (4.2.4.71)$$

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

$$I_d(\mathbf{H}) = N(\bar{f}^2 - \bar{f}^2) \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \alpha_{\nu\nu'} |_{\mathbf{nn}'} \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.71a)$$

In the simplest case of a binary system A, B

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

$$I_d(\mathbf{H}) = N c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \alpha_{\mathbf{nn}'} \times \exp\{2\pi i \mathbf{H}(\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.71b)$$

[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

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

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):

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

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

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

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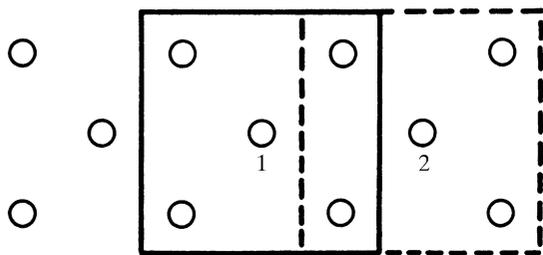


Fig. 4.2.4.1. Construction of the correlation function in the method of overlapping clusters.

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:

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

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

$$I_2 = 2\pi i c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{ H \cdot [F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB} \rangle] + K \cdot [y'] + L \cdot [z'] \} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \quad (4.2.4.79)$$

$$I_3 = c_A c_B (f_A - f_B)^2 (-2\pi)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \{ H^2 [F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA}^2 \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB}^2 \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB}^2 \rangle] + K^2 \cdot [y'^2] + L^2 \cdot [z'^2] + HK [F_{\mathbf{nn}'|AA} \langle (xy)_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle (xy)_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle (xy)_{\mathbf{nn}'|AB} \rangle] + KL [y'z'] + LH [z'x'] \} \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}. \quad (4.2.4.80)$$

With further abbreviations

$$\begin{aligned} \gamma_{\mathbf{nn}'|x} &= 2\pi (F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB} \rangle) \\ \gamma_{\mathbf{nn}'|y} &= \dots \\ \gamma_{\mathbf{nn}'|z} &= \dots \\ \delta_{\mathbf{nn}'|x} &= (-2\pi^2) (F_{\mathbf{nn}'|AA} \langle x_{\mathbf{nn}'|AA}^2 \rangle + F_{\mathbf{nn}'|BB} \langle x_{\mathbf{nn}'|BB}^2 \rangle + F_{\mathbf{nn}'|AB} \langle x_{\mathbf{nn}'|AB}^2 \rangle) \\ \delta_{\mathbf{nn}'|y} &= \dots \\ \delta_{\mathbf{nn}'|z} &= \dots \\ \varepsilon_{\mathbf{nn}'|xy} &= (-4\pi^2) (F_{\mathbf{nn}'|AA} \langle (xy)_{\mathbf{nn}'|AA} \rangle + F_{\mathbf{nn}'|BB} \langle (xy)_{\mathbf{nn}'|BB} \rangle + F_{\mathbf{nn}'|AB} \langle (xy)_{\mathbf{nn}'|AB} \rangle) \\ \varepsilon_{\mathbf{nn}'|yz} &= \dots \\ \varepsilon_{\mathbf{nn}'|zx} &= \dots \\ I_2 &= c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i (\gamma_{\mathbf{nn}'|x} + \gamma_{\mathbf{nn}'|y} + \gamma_{\mathbf{nn}'|z}) \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\} \\ I_3 &= c_A c_B (f_A - f_B)^2 \sum_{\mathbf{n}} \sum_{\mathbf{n}'} (\delta_{\mathbf{nn}'|x} H^2 + \delta_{\mathbf{nn}'|y} K^2 + \delta_{\mathbf{nn}'|z} L^2 + \varepsilon_{\mathbf{nn}'|xy} HK + \varepsilon_{\mathbf{nn}'|yz} KL + \varepsilon_{\mathbf{nn}'|zx} LH \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}). \end{aligned}$$

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:

$$\begin{aligned} Q_x &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} i \gamma_{\mathbf{nn}'|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ Q_y &= \dots; \quad Q_z = \dots; \\ R_x &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \delta_{\mathbf{nn}'|x} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ R_y &= \dots; \quad R_z = \dots; \\ S_{xy} &= \sum_{\mathbf{n}} \sum_{\mathbf{n}'} \varepsilon_{\mathbf{nn}'|xy} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{n} - \mathbf{n}')\}; \\ S_{yz} &= \dots; \quad S_{zx} = \dots \end{aligned}$$

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

$$I_2 = -N c_A c_B (f_A - f_B)^2 \sum_m \sum_n \sum_p (H \gamma_{|mn|_x} + \dots + \dots) \times \sin 2\pi (Hm + Kn + Lp). \quad (4.2.4.81)$$

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 $\delta, \varepsilon, R, S$ 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_{STO}, 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 (1950*a,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 $\text{Ag}_{1-x}\text{Mg}_x$ ($x = 0.15-0.20$) (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;

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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)

$$I_d^p = \{ \langle |F(\mathbf{H})|^2 \rangle - |\langle F(\mathbf{H}) \rangle|^2 \} \sum_i s_i \sin(2\pi H r_i) / (2\pi H r_i). \quad (4.2.4.82)$$

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

$$I_d^p = \alpha(1 - \alpha) \{ |f_2(\mathbf{H}) - f_1(\mathbf{H})|^2 \} \sum_i s_i \sin(2\pi H r_i) / (2\pi H r_i). \quad (4.2.4.83)$$

4.2.4.4.7. Small concentrations of defects

In the literature small concentrations are treated in terms of fluctuations of the functions $\pi_{\mathbf{nv}}$ 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

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

where $F_{\nu}(\mathbf{H})$ represents the difference structure factor of the ν th 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

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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 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: $\omega_l = 1, \dots, D$ (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 :

$$I(\mathbf{H}, t) = \sum_l \sum_{\nu} F_l(\mathbf{H}, t) F_{\nu}^+(\mathbf{H}, t) \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu})\} \quad (4.2.4.85)$$

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

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.)

$$I(\mathbf{H}, t) = \sum_l \sum_{\nu} \overline{F_l(\mathbf{H}, t) F_{\nu}^+(\mathbf{H}, t)} \times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{\nu})\}. \quad (4.2.4.85a)$$

Thermal averaging gives (*cf.* Chapter 4.1)

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

In the harmonic approximation $\exp\{2\pi i \mathbf{H} \cdot \Delta \mathbf{u}\}$ 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 $F_l F_{\nu}^+$ becomes

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

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B_k is equal to $\frac{1}{2}(2\pi\mathbf{H} \cdot \mathbf{u}_{lk})^2$ (Debye–Waller factor) and depends on the specific configuration ω_l . $D_{lk; l'k'} = \frac{(2\pi\mathbf{H} \cdot \mathbf{u}_{lk})(2\pi\mathbf{H} \cdot \mathbf{u}_{l'k'})}{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}$ includes all the correlations between positions, orientations and vibrations of the molecules.

Averaging over different configurations demands a knowledge of the orientational probabilities. The probability of finding molecule l in orientation ω_l is given by $p(\omega_l)$. The double probability $p(\omega_l, \omega_{l'})$ gives the probability of finding two molecules l, l' in different orientations ω_l and $\omega_{l'}$, respectively. In the absence of correlations between the orientations we have: $p(\omega_l, \omega_{l'}) = p(\omega_l)p(\omega_{l'})$. If correlations exist: $p(\omega_l, \omega_{l'}) = p(\omega_l)p'(\omega_l|\omega_{l'})$ where $p'(\omega_l|\omega_{l'})$ defines the conditional probability that molecule l has the orientation ω_l if molecule l' has the orientation $\omega_{l'}$. For long distances between l and l' $p'(\omega_l|\omega_{l'})$ tends to $p(\omega_{l'})$.

The difference $\Delta(\omega_l|\omega_{l'}) = p'(\omega_l|\omega_{l'}) - p(\omega_{l'})$ characterizes, therefore, the degree of short-range orientational correlation. Note that this formalism corresponds fully to the $p_{\mu}, p_{\mu\mu'}$ used in the context of translational disorder.

The average structure factor, sometimes called averaged form factor, of the molecule is given by

$$\langle F_l \rangle = \sum_{\omega_l} p(\omega_l) F_l(\omega_l). \quad (4.2.4.89)$$

(a) Negligible correlations between vibrations of different molecules (Einstein model):

$$D_{lk; l'k'} = 0 \text{ for } l \neq l'.$$

From (4.2.4.88) it follows (the prime symbol takes the Debye–Waller factor into account):

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ N \left\{ \sum_k \sum_{k'} \sum_{\omega_l} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk; l'k'}\} - |\langle F' \rangle|^2 \left. \right\} \\ &+ N \sum_{\Delta l \neq 0} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\}. \end{aligned} \quad (4.2.4.90)$$

$L(\mathbf{H})$ is the reciprocal lattice of the well defined ordered lattice. The first term describes Bragg scattering from an averaged structure. The second term governs the diffuse scattering in the absence of short-range orientational correlations. The last term takes the correlation between the orientations into account.

If rigid molecules with centre-of-mass translational displacements and negligible librations are assumed, which is a first approximation only, $|\langle F \rangle|^2$ is no longer affected by a Debye–Waller factor.

In this approximation the diffuse scattering may therefore be separated into two parts:

$$N(\langle F^2 \rangle - |\langle F' \rangle|^2) = N(F^2 - |\langle F \rangle|^2) + N(|\langle F \rangle|^2 - |\langle F' \rangle|^2) \quad (4.2.4.91)$$

with

$$\begin{aligned} \langle F^2 \rangle &= \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} f_k(\omega_l) f_{k'}(\omega_{l'}) p(\omega_l) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\}. \end{aligned} \quad (4.2.4.92)$$

The first term in (4.2.4.91) gives the scattering from equilibrium fluctuations in the scattering from individual molecules (diffuse scattering without correlations), the second gives the contribution from the centre-of-mass thermal vibrations of the molecules.

(b) If intermolecular correlations between the molecules cannot be neglected, the final intensity expression for diffuse scattering is very complicated. In many cases these correlations are caused by dynamical processes (see Chapter 4.1). A simplified treatment assumes the molecule to be a rigid body with a centre-of-mass displacement \mathbf{u}_l and neglects vibrational–librational and librational–librational correlations: $D_{l; l'} = \frac{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}{(2\pi\mathbf{H} \cdot \mathbf{u}_l)(2\pi\mathbf{H} \cdot \mathbf{u}_{l'})}$ ($l \neq l'$). The following expression approximately holds:

$$\begin{aligned} \overline{\langle I \rangle} &= N^2 |\langle F' \rangle|^2 L(\mathbf{H}) \\ &+ \left\langle \sum_l \sum_{l'} F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \exp\{D_{l; l'}\} \right\rangle \{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \\ &+ N \left\{ \sum_{\omega_l} \sum_{k, k'} p(\omega_l) f_k f_{k'} \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \right. \\ &\times \exp\{D_{lk; l'k'}\} - \sum_{\omega_l} \sum_{\omega_{l'}} \sum_k \sum_{k'} p(\omega_l) p(\omega_{l'}) f_k f_{k'} \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \\ &\times \exp\{D_{lk; l'k'}\} \left. \right\} + \sum_{l \neq l'} \sum_{\omega_l} \sum_{\omega_{l'}} p(\omega_l) \Delta(\omega_l|\omega_{l'}) \\ &\times F'_l(\omega_l) F_{l'}^+(\omega_{l'}) \\ &\times \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_l - \mathbf{r}_{l'})\} \exp\{D_{l; l'}\}. \end{aligned} \quad (4.2.4.93)$$

Again the first term describes Bragg scattering and the second corresponds to the average thermal diffuse scattering in the disordered crystal. Because just one molecule belongs to one unit cell only acoustic waves contribute to this part. To an approximation, the result for an ordered crystal may be used by replacing F by $\langle F' \rangle$ [Chapter 4.1, equation (4.1.3.4)]. The third term corresponds to random-disorder diffuse scattering. If librations are neglected this term may be replaced by $N(\langle F^2 \rangle - \langle F \rangle^2)$. The last term in (4.2.4.93) describes space correlations. Omission of $\exp\{D_{l; l'}\}$ or expansion to $\sim (1 + D_{l; l'})$ are further simplifying approximations.

In either (4.2.4.90) or (4.2.4.93) the diffuse-scattering part depends on a knowledge of the conditional probability $\Delta(\omega_l|\omega_{l'})$ and the orientational probability $p(\omega_l)$. The latter may be found, at least in principle, from the average structure factor.

4.2.4.5.2. Rotational structure (form) factor

In certain cases and with simplifying assumptions, $\langle F \rangle$ [equation (4.2.4.89)] and $\langle \Delta F^2 \rangle$ [equation (4.2.4.92)] may be calculated. Assuming only one molecule per unit cell and treating the molecule as a rigid body, one derives from the structure factor of an ordered crystal F_l

$$\langle F \rangle = \sum_k f_k \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \quad (4.2.4.94)$$

and

$$\begin{aligned} \langle \Delta F^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} [\langle \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \rangle \\ &- \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{l'k'}\} \rangle]. \end{aligned} \quad (4.2.4.95)$$

If the molecules have random orientation in space the following expressions hold [see, *e.g.*, Dolling *et al.* (1979)]:

$$\langle F \rangle = \sum_k f_k j_0(\mathbf{H} \cdot \mathbf{r}_k) \quad (4.2.4.96)$$

$$\begin{aligned} \langle |\Delta F|^2 \rangle &= \sum_k \sum_{k'} f_k f_{k'} \{ j_0(\mathbf{H} \cdot (\mathbf{r}_k - \mathbf{r}_{k'})) \\ &- j_0(\mathbf{H} \cdot \mathbf{r}_k) j_0(\mathbf{H} \cdot \mathbf{r}_{k'}) \}. \end{aligned} \quad (4.2.4.97)$$

$j_0(z)$ is the zeroth order of the spherical Bessel functions and describes an atom k uniformly distributed over a shell of radius r_k .

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In practice the molecules perform more or less finite librations about the main orientation. The structure factor may then be found by the method of symmetry-adapted functions [see, *e.g.*, Press (1973), Press & Hüller (1973), Dolling *et al.* (1979), Prandl (1981, and references therein)].

$$\langle F \rangle = \sum_k f_k 4\pi \sum_{\nu} \sum_{\mu=-\nu}^{+\nu} i^{\nu} j_{\nu}(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{(k)} Y_{\nu\mu}(\theta, \varphi). \quad (4.2.4.98)$$

$j_{\nu}(z)$ is the ν th order of spherical Bessel functions, the coefficients $C_{\nu\mu}^{(k)}$ characterize the angular distribution of \mathbf{r}_k , $Y_{\nu\mu}(\theta, \varphi)$ are the spherical harmonics where $|\mathbf{H}|, \theta, \varphi$ denote polar coordinates of \mathbf{H} .

The general case of an arbitrary crystal, site and molecular symmetry and the case of several symmetrically equivalent orientationally disordered molecules per unit cell are treated by Prandl (1981); an example is given by Hohlwein *et al.* (1986). As mentioned above, cubic plastic crystals are common and therefore mostly studied up to now. The expression for $\langle F \rangle$ may then be formulated as an expansion in cubic harmonics, $K_{\nu\mu}(\theta, \varphi)$:

$$\langle F \rangle = \sum_k f_k 4\pi \sum_{\nu} \sum_{\mu} i^{\nu} j_{\nu}(\mathbf{H} \cdot \mathbf{r}_k) C'_{\nu\mu} K_{\nu\mu}(\theta, \varphi). \quad (4.2.4.99)$$

($C'_{\nu\mu}$ are modified expansion coefficients.)

Taking into account isotropic centre-of-mass translational displacements, which are not correlated with the librations, we obtain:

$$\langle F' \rangle = \langle F \rangle \exp\left\{-\frac{1}{6} H^2 \langle U^2 \rangle\right\}. \quad (4.2.4.100)$$

U is the mean-square translational displacement of the molecule. Correlations between translational and vibrational displacements are treated by Press *et al.* (1979).

Equivalent expressions for crystals with symmetry other than cubic may be found from the same concept of symmetry-adapted functions [tables are given by Bradley & Cracknell (1972)].

4.2.4.5.3. Short-range correlations

The final terms in equations (4.2.4.90) and (4.2.4.93) concern correlations between the orientations of different molecules. Detailed evaluations need a knowledge of a particular model. Examples are compounds with nitrate groups (Wong *et al.*, 1984; Lefebvre *et al.*, 1984), CBr_4 (More *et al.*, 1980, 1984), and many others (see Sherwood, 1979). The situation is even more complicated when a modulation wave with respect to the occupation of different molecular orientations is superimposed. A limiting case would be a box-like function describing a pattern of domains. Within one domain all molecules have the same orientation. This situation is common in ferroelectrics where molecules exhibit a permanent dipole moment. The modulation may occur in one or more directions in space. The observed intensity in this type of orientationally disordered crystal is characterized by a system of more or less diffuse satellite reflections. The general scattering theory of a crystal with occupational modulation waves follows the same lines as outlined in Section 4.2.3.1.

4.2.5. Measurement of diffuse scattering

To conclude this chapter experimental aspects are summarized which are specifically important in diffuse-scattering work. The summary is restricted to film methods commonly used in laboratories and (X-ray or neutron) diffractometer measurements. Sophisticated special techniques and instruments at synchrotron facilities and reactors dedicated to diffuse-scattering work are not described here. The full merit of these machines may be assessed

after inspection of corresponding user handbooks which are available upon request. Also excluded from this section are instruments and methods related to diffuse scattering at low angles, *i.e.* small-angle scattering techniques. Although no fundamental differences exist between an X-ray experiment in a laboratory and at a synchrotron facility, some specific points have to be considered in the latter case. These are discussed by Matsubara & Georgopoulos (1985), Oshima & Harada (1986), and Ohshima *et al.* (1986).

Generally, diffuse scattering is weak in comparison with Bragg scattering, anisotropically and inhomogeneously distributed in reciprocal space, elastic, inelastic, or quasi-elastic in origin. It is frequently related to more than one structural element, which means that different parts may show different behaviour in reciprocal space and/or on an energy scale. Therefore special care has to be taken concerning the following points: (1) type of experiment: X-rays or neutrons, film or diffractometer/spectrometer, single crystal or powder; (2) strong sources; (3) best choice of wavelength (or energy) of incident radiation if no 'white' technique is used; (4) monochromatic and focusing techniques; (5) sample environment and background reduction; (6) resolution and scanning procedure in diffractometer or densitometer recording.

On undertaking an investigation of a disorder problem by an analysis of the diffuse scattering an overall picture should first be recorded by X-ray diffraction experiments. Several sections through reciprocal space help to define the problem. For this purpose film methods are preferable. Cameras with relatively short crystal-film distances avoid long exposure times. Unfortunately, there are some disorder problems which cannot be tackled by X-ray methods. X-rays are rather insensitive for the elucidation of disorder problems where light atoms in the presence of heavy atoms play the dominant role, or when elements are involved which scarcely differ in X-ray scattering amplitudes (*e.g.* Al/Si/Mg). In these cases neutrons have to be used at an early stage. If a significant part of the diffuse scattering is suspected not to be of static origin concomitant purely elastic, quasi-elastic or inelastic neutron experiments have to be planned from the very beginning.

Because diffuse scattering is usually weak, intense radiation sources are needed, whereas the background level should be kept as low as possible. Coming to the background problem later, we should make some brief remarks concerning sources. Even a normal modern X-ray tube is a stronger source, defined by the flux density from an anode (number of photons $\text{cm}^{-2} \text{s}^{-1}$), than a reactor with the highest available flux. For this reason most experimental work which can be performed with X-rays should be. Generally the characteristic spectrum will be used, but special methods have been developed where the white X-ray spectrum is of interest (see below). A most powerful source in this respect is a modern synchrotron storage ring (see, *e.g.*, Kunz, 1979). With respect to rotating anodes one should bear in mind not only the power but also the flux density, because there is little merit for a broad focus in diffuse-scattering work (separation of sharp and diffuse scattering). One can suppose that synchrotron radiation in the X-ray range will also play an important role in the field of monochromatic diffraction methods, owing to the extremely high brilliance of these sources (number of quanta $\text{cm}^{-2}, \text{sr}^{-1}, \text{s}^{-1}$ and wavelength interval). Diffuse neutron-diffraction work may only be performed on a high- or medium-flux reactor. Highly efficient monochromator systems are necessary. In combination with time-of-flight neutron methods pulsed sources are nowadays equivalent to reactors (Windsor, 1982).

If film and (X-ray) diffractometer methods are compared, film techniques are highly recommended at an early stage to give a general survey of the disorder problem. Routine X-ray techniques such as rotation photographs, Weissenberg or precession techniques may be used. The Weissenberg method is preferred to the

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precession method in most cases because of the comparatively larger coverage of reciprocal space (with the same wavelength). The drawback of a distorted image of the reciprocal space may be compensated by digitizing the film blackening *via* a densitometer recording and subsequent plotting. With this procedure a distorted section through the reciprocal lattice may be transformed into a form suitable for easy interpretation (Welberry, 1983).

Frequently used are standing-crystal techniques in combination with monochromatic radiation, usually called monochromatic Laue techniques (see, *e.g.*, Flack, 1970). The Noromosaic technique (Jagodzinski & Korekawa, 1973) is characterized by a convergent monochromatic beam which simulates an oscillation photograph over a small angular range. Heavily overexposed photographs, with respect to Bragg scattering, allow for sampling of diffuse intensity if a crystal is oriented in such a way that there is a well defined section between the Ewald sphere and the diffuse phenomenon under consideration. By combining single Noromosaic photographs, Weissenberg patterns can be simulated. This relatively tedious way of comparison with a true Weissenberg photograph is often unavoidable because the heavily overexposed Bragg peaks obscure weak diffuse phenomena over a considerable area of a photograph. Furthermore, standing pictures are pointwise measurements in comparison with the normal continuous pattern with respect to the crystal setting. Long-exposure Weissenberg photographs are therefore not equivalent to a smaller set of standing photographs. In this context it should be mentioned that a layer-line screen has not only the simple function of a selecting diaphragm, but the gap width determines the resolution volume within which diffuse intensity is collected (Welberry, 1983). For further discussion of questions of resolution see below. Single-crystal diffractometer measurements, either in the X-ray or in the neutron case, are frequently adopted for quantitative measurements of diffuse intensities. Microdensitometer recording of X-ray films is an equivalent method, incorporating corrections for background and other factors into this procedure. A comparison of Weissenberg and diffractometer methods for the measurement of diffuse scattering is given by Welberry & Glazer (1985).

In the case of powder-diffractometer experiments preferred orientations/textures could lead to a complete misidentification of the problem. Single-crystal experiments are preferable in some respect, because diffuse phenomena in a powder diagram may be analysed only after an idea about the disorder has been obtained and only in special cases. Nevertheless, high-resolution powder investigations give quick supporting information, *e.g.* about superlattice peaks, split reflections, lattice strains, domain size effects, lattice-constant change related to a disorder effect *etc.*

Before starting an experiment of any kind, one should specify the optimum wavelength. This is important with respect to the problem to be solved: *e.g.*, point defects cause diffuse scattering to fall off with increasing scattering vector; short-range ordering between clusters causes broad peaks corresponding to large d spacings; lattice-relaxation processes induce a broadening of the interferences (Huang scattering); or static modulation waves with long periods give rise to satellite scattering close to Bragg peaks. In all these cases a long wavelength is preferable. On the other hand, a shorter wavelength is needed if diffuse phenomena are structured in a sense that broad peaks are observable up to large reciprocal vectors, or diffuse streaks or planes have to be recorded up to high values of the scattering vector in order to decide between different models. The λ^3 -dependence of the scattered intensity, in the framework of the kinematical theory, is a crucial point for exposure or data-acquisition times. Moreover, the accuracy with which an experiment can be carried out suffers from a short wavelength: generally, momentum as well as energy resolution are lower. For a quantitative estimate detailed considerations of resolution in reciprocal (and energy) space are needed. Special attention must

be paid to absorption phenomena, in particular when (in the X-ray case) an absorption edge of an element of the sample is close to the wavelength used. $\lambda \sim 0.91 \text{ \AA}$ must be avoided in combination with film methods owing to the K edge of Br. Strong fluorescence scattering may completely obscure weak diffuse-scattering phenomena. In comparison with X-rays, the generally lower absorption coefficients of neutrons of any wavelength makes absolute measurements easier. This also allows the use of larger sample volumes, which is not true in the X-ray case. An extinction problem does not exist in diffuse-scattering work. In particular, the use of a long wavelength is profitable when the main diffuse contributions can be recorded within an Ewald sphere as small as the Bragg cut-off of the sample: $\lambda = 2d_{\max}$; a contamination by Bragg scattering can then be avoided.

This is also advantageous from a different point of view: because the contribution of thermal diffuse scattering increases with increasing scattering vector \mathbf{H} , the relative amount of this component becomes negligibly small within the first reciprocal cell.

Highly monochromatic radiation should be used in order to eliminate broadening effects due to the wavelength distribution. Focusing monochromators help to overcome the lack of luminosity. A focusing technique, in particular a focusing camera geometry, is very helpful for deciding between geometrical broadening and 'true' diffuseness. With good success a method is used where in a monochromatic divergent beam the sample is placed with its selected axis lying in the scattering plane of the monochromator (Jagodzinski, 1968). The specimen is fully embedded in the incident beam which is focused onto the film. By this procedure the influence of the sample size is suppressed in one dimension. In an oscillation photograph a high resolution perpendicular to the diffuse layer lines may thus be achieved.

A serious problem is a careful suppression of background scattering. Incoherent X-ray scattering as an inherent property of a sample occurs as continuous blackening in the case of fluorescence, or as scattering at high 2θ angles owing to Compton scattering or 'incoherent' inelastic effects. Protecting the film by a thin Al or Ni foil is of some help against fluorescence, but also attenuates the diffuse intensity. Scratching the film emulsion after the exposure from the 'front' side of the film is another possibility for reducing the relative amount of the lower-energy fluorescence radiation. Obviously, energy-dispersive counter methods are highly efficient in this case (see below). Air scattering produces a background at low 2θ angles which may easily be avoided by special slit systems and evacuation of the camera.

In X-ray or neutron diffractometer measurements incoherent and multiple scattering contribute to a background which varies only slowly with 2θ and can be subtracted by linear interpolation or fitting a smooth curve, or can even be calculated quantitatively and then subtracted. In neutron diffraction there are rare cases when monoisotopic and 'zero-spin' samples are available and, consequently, the corresponding incoherent scattering part vanishes completely. In some cases a separation of coherent and incoherent neutron scattering is possible by polarization analysis (Gerlach *et al.*, 1982). An 'empty' scan can take care of instrumental background contributions. Evacuation or controlled-atmosphere studies need a chamber which may give rise to spurious scattering. This can be avoided if no part of the vacuum chamber is hit by the primary beam. The problem is less serious in neutron work. Mounting a specimen, *e.g.*, on a silica fibre with cement, poorly aligned collimators or beam catchers are further sources. Sometimes a specimen has to be enclosed in a capillary which will always be hit by the incident beam. Careful and tedious experimental work is necessary in the case of low- and high-temperature (or -pressure) investigations which have to be carried out in many disorder problems. Whereas the experimental situation is again less serious in neutron scattering, there are large problems with scattering from

4. DIFFUSE SCATTERING AND RELATED TOPICS

walls and containers in X-ray work. Most of the X-ray investigations have therefore been made on quenched samples. Because TDS is dominating at high temperatures, also in the presence of a static disorder problem, the quantitative separation can hardly be carried out in the case of high experimental background. Calculation and subtraction of the TDS is possible in principle, but difficult in practice.

A quantitative analysis of diffuse-scattering data is essential for a definite decision about a disorder model. By comparison of calculated and corrected experimental data the magnitudes of the parameters of the structural disorder model may be derived. A careful analysis of the data requires, therefore, corrections for polarization (X-ray case), absorption and resolution. These may be performed in the usual way for polarization and absorption. Very detailed considerations, however, are necessary for the question of instrumental resolution which depends, in addition to other factors, on the scattering angle and implies intensity corrections analogous to the Lorentz factor used in structure analysis from sharp Bragg reflections.

Resolution is conveniently described by a function, $R(\mathbf{H} - \mathbf{H}_0)$, which is defined as the probability of detecting a photon or neutron with momentum transfer $h\mathbf{H} = h(\mathbf{k} - \mathbf{k}_0)$ when the instrument is set to measure \mathbf{H}_0 . This function R depends on the instrumental parameters (collimations, mosaic spread of monochromator, scattering angle) and the spectral width of the source. Fig. 4.2.5.1 shows a schematic sketch of a diffractometer setting. Detailed considerations of resolution volume in X-ray diffractometry are given by Sparks & Borie (1966). If a triple-axis (neutron) instrument is used, for example in a purely elastic configuration, the set of instrumental parameters is extended by the mosaic of the analyser and the collimations between analyser and detector (see Chapter 4.1).

If photographic (X-ray) techniques are used, the detector aperture is controlled by the slit width of the microdensitometer. A general formulation of R in neutron diffractometry is given by Cooper & Nathans (1968):

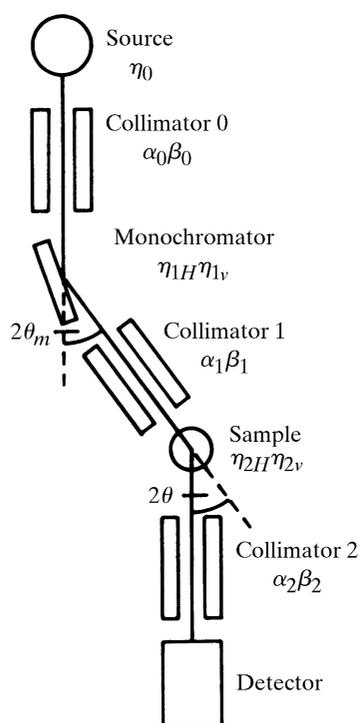


Fig. 4.2.5.1. Schematic sketch of a diffractometer setting.

$$R'(\mathbf{H} - \mathbf{H}_0) = R'_0 \exp \left\{ -\frac{1}{2} \sum_k \sum_l M'_{kl} \Delta H_k \Delta H_l \right\}. \quad (4.2.5.1)$$

Gaussians are assumed for the mosaic distributions and for the transmission functions the parameters are involved in the coefficients R'_0 and M'_{kl} .

The general assumption of Gaussians is not too serious in the X-ray case (Iizumi, 1973). Restrictions are due to absorption which makes the profiles asymmetric. Box-like functions are considered to be better for the spectral distribution or for large apertures (Boysen & Adlhart, 1987). These questions are treated in some detail by Klug & Alexander (1954). The main features, however, may also be derived by the Gaussian approximation. In practice the function R may be obtained either by calculation from the known instrumental parameters or by measuring Bragg peaks of a perfect unstrained crystal. In the latter case [cf. equation (4.2.5.2)] the intensity profile is given solely by the resolution function. A normalization with the Bragg intensities is also useful in order to place the diffuse-scattering intensity on an absolute scale.

In single-crystal diffractometry the measured intensity is given by the convolution product of $d\sigma/d\Omega$ with R ,

$$I(\mathbf{H}_0) = \int \frac{d\sigma}{d\Omega}(\mathbf{H}) \cdot R(\mathbf{H} - \mathbf{H}_0) d\mathbf{H}, \quad (4.2.5.2)$$

where $d\sigma/d\Omega$ describes the scattering cross section for the disorder problem. In more accurate form the mosaic of the sample has to be included:

$$\begin{aligned} I(\mathbf{H}_0) &= \int \frac{d\sigma}{d\Omega}(\mathbf{H} - \Delta\mathbf{k}) \cdot \eta(\Delta\mathbf{k}) R(\mathbf{H} - \mathbf{H}_0) d\mathbf{H} d(\Delta\mathbf{k}) \\ &= \int \frac{d\sigma}{d\Omega}(\mathbf{H}') \cdot R'(\mathbf{H}' - \mathbf{H}_0) d\mathbf{H}'. \end{aligned} \quad (4.2.5.2a)$$

$R'(\mathbf{H}' - \mathbf{H}_0) = \int \eta(\Delta\mathbf{k}) R(\mathbf{H}' + \Delta\mathbf{k} - \mathbf{H}_0) d(\Delta\mathbf{k})$. $\eta(\Delta\mathbf{k})$ describes the mosaic block distribution around a most probable vector \mathbf{k}_0 : $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_0$; $\mathbf{H}' = \mathbf{H} - \Delta\mathbf{k}$.

In formulae (4.2.5.1) and (4.2.5.2) all factors independent of 2θ are neglected. All intensity expressions have to be calculated from equations (4.2.5.2) or (4.2.5.2a). In the case of a dynamical disorder problem, *i.e.* when the differential cross section also depends on energy transfer $\hbar\omega$, the integration must be extended over energy.

The intensity variation of diffuse peaks with 2θ was studied in detail by Yessik *et al.* (1973). In principle all special cases are included there. In practice, however, some important simplifications can be made if $d\sigma/d\Omega$ is either very broad or very sharp compared with R , *i.e.* for Bragg peaks, sharp streaks, 'thin' diffuse layers or extended 3D diffuse peaks (Boysen & Adlhart, 1987).

In the latter case the cross section $d\sigma/d\Omega$ may be treated as nearly constant over the resolution volume so that the corresponding 'Lorentz' factor is independent of 2θ :

$$L_{3D} = 1. \quad (4.2.5.3)$$

For a diffuse plane within the scattering plane with very small thickness and slowly varying cross section within the plane, one derives for a point measurement in the plane:

$$L_{2D, \parallel} = (\beta_1^2 + \beta_2^2 + \eta_{2v}^2 - \sin^2 \theta)^{-1/2}, \quad (4.2.5.4)$$

exhibiting an explicit dependence on θ ($\beta_1, \beta_2, \eta_{2v}$ determining an effective vertical divergence before the sample, the divergence before the detector and the vertical mosaic spread of the sample, respectively).

In the case of *relaxed* vertical collimations $\beta_1, \beta_2 \gg \eta_{2v}$

$$L_{2D, \parallel} = (\beta_1^2 + \beta_2^2)^{-1/2}, \quad (4.2.5.4a)$$

i.e. again independent of θ .

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

Scanning across the diffuse layer in a direction perpendicular to it one obtains an integrated intensity which is also independent of 2θ . This is even true if approximations other than Gaussians are used.

If, on the other hand, an equivalent diffuse plane is positioned perpendicular to the scattering plane, the equivalent expression for $L_{2D, \perp}$ of a point measurement is given by

$$L_{2D, \perp} \simeq [4\eta_{2H}^2 \sin^2 \theta \cos^2 \psi + \alpha_2^2 \sin^2(\psi - \theta) + \sin^2(\psi + \theta) + 4\eta_0' \sin^2 \theta \sin^2 \psi - 4\alpha_1'' \sin \theta \sin \psi \sin(\theta + \psi)], \quad (4.2.5.5)$$

where ψ gives the angle between the line of intersection between the diffuse and the scattering plane and the vector \mathbf{H}_0 . The coefficients η_{2H} , α_2 , α_1' , α_1'' , η are either instrumental parameters or functions of them, defining horizontal collimations and mosaic spreads. In the case of a (sharp) X-ray line (produced, for example, by filtering) the last two terms in equation (4.2.5.5) vanish.

The use of integrated intensities from individual scans perpendicular to the diffuse plane, now carried out within the scattering plane, again gives a Lorentz factor independent of 2θ .

In the third fundamental special case, diffuse streaking along one reciprocal direction within the scattering plane (narrow cross section, slowly varying intensity along the streak), the Lorentz factor for a point measurement may be expressed by the product

$$L_{1D, \parallel} \simeq L_{2D, \parallel} L_{2D, \perp}, \quad (4.2.5.6)$$

where ψ now defines the angle between the streak and \mathbf{H}_0 . The integrated intensity taken from an H scan perpendicular to the streak has to be corrected by a Lorentz factor which is equal to $L_{2D, \parallel}$ [equation (4.2.5.4)]. In the case of a diffuse streak perpendicular to the scattering plane a relatively complicated equation holds for the corresponding Lorentz factor (Boysen & Adlhart, 1987). Again more simple expressions hold for integrated intensities from H scans perpendicular to the streaks. Such scans may be performed in the radial direction (corresponding to a θ - 2θ scan):

$$L_{1D, \perp, \text{rad}} = (4\eta_{2H}^2 + \alpha_2^2 + \alpha_1'^2)^{-1/2} \cdot 1/\sin \theta \quad (4.2.5.7)$$

or perpendicular to the radial direction (within the scattering plane) (corresponding to an ω scan):

$$L_{1D, \perp, \text{per}} = (\alpha_2^2 + \alpha_1'^2 + 4\eta_0' \tan^2 \theta - 4\alpha_1'' \tan \theta)^{-1/2} \cdot 1/\cos \theta \quad (4.2.5.8)$$

Note that only the radial scan yields a simple θ dependence ($\sim 1/\sin \theta$).

From these considerations it is recommended that integrated intensities from scans perpendicular to a diffuse plane or a diffuse streak should be used in order to extract the disorder cross sections. For other scan directions, which make an angle α with the intersection line (diffuse plane) or with a streak, the L factors are simply: $L_{2D, \perp}/\sin \alpha$ and $L_{1D, \perp}/\sin \alpha$, respectively.

One point should be emphasized: since in a usual experiment the integration is performed over an angle $\Delta\omega$ via a general $\delta\omega$: ($g\delta 2\theta$) scan, an additional correction factor arises:

$$\Delta\omega/\Delta\mathbf{H}_\beta = \sin(\beta + \theta)/(\mathbf{k}_0 \sin 2\theta). \quad (4.2.5.9)$$

β is the angle between \mathbf{H}_0 and the scan direction \mathbf{H}_β ; $g = (\tan \beta + \tan \theta)/(2 \tan \theta)$ defines the coupling ratio between the rotation of the crystal around a vertical axis and the rotation of the detector shaft. Most frequently used are the so-called 1:2 and ω -scan techniques where $\beta = 0$ and 90° , respectively.

It should be mentioned that the results in the neutron case are restricted to the elastic diffuse part, since in a diffractometer measurement the inelastic part deserves special attention concerning the integration over energy by the detector (Tucciarone *et al.*,

1971; Grabcev, 1974). If a triple-axis instrument is used, the collimations α_2 and β_2 have to be replaced by effective values after the sample owing to the analyser system.

In order to optimize a single-crystal experiment, the scan direction and also the instrumental collimations should be carefully chosen according to the anisotropy of the diffuse phenomenon. If the variation of $d\sigma/d\Omega$ is appreciable along a streak, the resolution should be held narrow in one direction and relaxed in the other to gain intensity and the scans should be performed perpendicular to that direction. If the variation is smooth the sharpest signal is measured by a scan perpendicular to the streak. In any case, a good knowledge of the resolution and its variation with 2θ is helpful.

Even the diffuse background in powder diagrams contains valuable information about disorder. Only in very simple cases can a model be deduced from a powder pattern alone; however, a refinement of a known disorder model can favourably be carried out, *e.g.* the temperature dependence may be studied. On account of the intensity integration the ratio of diffuse intensity to Bragg intensity is enhanced in a powder pattern. Moreover, a powder pattern contains, in principle, all the information about the sample and might thus reveal more than single-crystal work.

The quantitative calculation of a diffuse background is also helpful in combination with Rietveld's (1969) method for refining an averaged structure by fitting (powder) Bragg reflections. In particular, for highly anisotropic diffuse phenomena characteristic asymmetric line shapes occur.

The calculation of these line shapes is treated in the literature, mostly neglecting the instrumental resolution (see, *e.g.*, Warren, 1941; Wilson, 1949; Jones, 1949; and de Courville-Brenasin *et al.*, 1981). This is not justified if the variation of the diffuse intensity becomes comparable with that of the resolution function as is often the case in neutron diffraction. It may be incorporated by taking advantage of a resolution function of a powder instrument (Caglioti *et al.*, 1958). A detailed analysis of diffuse peaks is given by Yessik *et al.* (1973), the equivalent considerations for diffuse planes and streaks by Boysen (1985). The case of 3D random disorder (incoherent neutron scattering, monotonous Laue scattering, averaged TDS, multiple scattering or short-range-order modulations) is treated by Sabine & Clarke (1977).

In polycrystalline samples the cross section has to be averaged over all orientations (n_c = number of crystallites in the sample):

$$\frac{d\sigma_p}{d\Omega}(\mathbf{H}') = \frac{n_c}{H^2} \int \frac{d\sigma}{d\Omega}(\mathbf{H}') R'(|\mathbf{H}'| - |\mathbf{H}_0|) d\mathbf{H}' \quad (4.2.5.10)$$

and this averaged cross section enters the relevant expressions for the convolution product with the resolution function.

A general intensity expression may be written as (Yessik *et al.*, 1973):

$$I_n(\mathbf{H}_0) = P \sum_{\tau} m(\tau) A_n \Phi_n(\mathbf{H}_0, \tau). \quad (4.2.5.11)$$

P denotes a scaling factor depending on the instrumental luminosity, τ the shortest distance to the origin of the reciprocal lattice, $m(\tau)$ the corresponding symmetry-induced multiplicity, A_n contains the structure factor of the structural units and the type of disorder, and Φ_n describes the characteristic modulation of the diffuse phenomenon of dimension n in the powder pattern. These expressions are given below with the assumption of Gaussian line shapes of width D for the narrow extension(s). The formulae depend on a factor $M = A_{1/2}(4k_1^2 - H_0^2)/(32 \ln 2)$, where $A_{1/2}$ describes the dependence of the Bragg peaks on the instrumental parameters U , V , W (see Caglioti *et al.*, 1958),

$$A_{1/2}^2 = U \tan^2 \theta + V \tan \theta + W. \quad (4.2.5.12)$$

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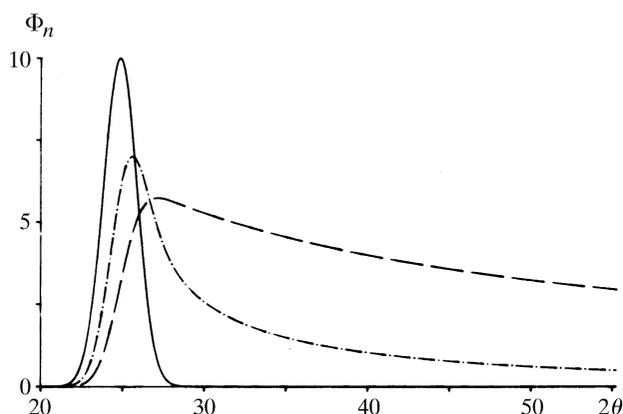


Fig. 4.2.5.2. Line profiles in powder diffraction for sharp and diffuse reflections; peaks (full line), continuous streaks (dot-dash lines) and continuous planes (broken lines). For explanation see text.

(a) *Isotropic diffuse peak around τ*

$$\Phi_0 = [2\pi(M^2 + D^2)]^{-1/2} \cdot 1/\tau^2 \times \exp\{-\mathbf{H}_0 - \tau\}^2/2(M^2 + D^2)\}. \quad (4.2.5.13)$$

The moduli $|\mathbf{H}_0|$ and $|\tau|$ enter the exponential, *i.e.* the variation of $d\sigma/d\Omega$ along $|\mathbf{H}_0|$ is essential. For broad diffuse peaks ($M \ll D$) the angular dependence is due to $1/\tau^2$, *i.e.* proportional to $1/\sin^2 \theta$. This result is valid for diffuse peaks of any shape.

(b) *Diffuse streak*

$$\Phi_1 = 2\pi(M^2 + D^2)^{-1/2} \int (\tau^2 + q^2)^{-1/2} \times \exp\{-\mathbf{H}_0 - \sqrt{\tau^2 + q^2}/2(M^2 + D^2)\} dq. \quad (4.2.5.14)$$

The integral has to be evaluated numerically. If $(M^2 + D^2)$ is not too large, the term $1/k_0^2 = 1/(\tau^2 + q^2)$ varies only slowly compared to the exponential term and may be kept outside the integral, setting it approximately to $1/H_0^2$.

(c) *Diffuse plane (with $r^2 = q_x^2 + q_y^2$)*

$$\Phi_2 = (M^2 + D^2)^{-1/2} \int r^2/(\tau^2 + r^2) \times \exp\{-\mathbf{H}_0 - \sqrt{\tau^2 + r^2}/2(M^2 + D^2)\} dr. \quad (4.2.5.15)$$

With the same approximation as in (b) the expression may be

simplified to

$$\Phi_2 = \pi/\mathbf{H}_0 [1 - \text{erf}\{(\tau - \mathbf{H}_0)/\sqrt{2(M^2 + D^2)}\} + 1/\mathbf{H}_0^2 \sqrt{2\pi(M^2 + D^2)} \times \exp\{-(\mathbf{H}_0 - \tau)^2/2(M^2 + D^2)\}]. \quad (4.2.5.16)$$

(d) *Slowly varying diffuse scattering in three dimensions*

$\Phi_3 = \text{constant}$.

Consequently, the intensity is directly proportional to the cross section. The characteristic functions Φ_0 , Φ_1 and Φ_2 are shown in Fig. 4.2.5.2 for equal values of τ and D . Note the relative peak shifts and the high-angle tail.

Techniques for the measurement of diffuse scattering using a *white* spectrum are common in neutron diffraction. Owing to the relatively low velocity of thermal or cold neutrons, time-of-flight (TOF) methods in combination with time-resolving detector systems, placed at a fixed angle 2θ , allow for a simultaneous recording along a radial direction through the origin of reciprocal space (see, *e.g.*, Turberfield, 1970; Bauer *et al.*, 1975). The scan range is limited by the Ewald spheres corresponding to λ_{max} and λ_{min} , respectively. With several such detector systems placed at different angles, several scans may be carried out simultaneously during one neutron pulse. There is a renaissance of these methods in combination with high-flux pulsed neutron sources.

An analogue of neutron TOF diffractometry in the X-ray case is a combination of a white source of X-rays and an energy-dispersive detector. This technique, which has been known in principle for a long time, suffered from relatively weak white sources. With the development of high-power X-ray generators or the powerful synchrotron source this method has become highly interesting in recent times. Its use in diffuse-scattering work (in particular, resolution effects) is discussed by Harada *et al.* (1984).

Valuable developments with a view to diffuse-scattering work are multidetectors (see, *e.g.*, Haubold, 1975) and position-sensitive detectors for X-rays (Arndt, 1986a) and neutrons (Convert & Forsyth, 1983). A linear position-sensitive detector allows one to record a large amount of data at the same time, which is very favourable in powder work and also in diffuse scattering with single crystals. By combining a linear position-sensitive detector and the TOF method a whole area in reciprocal space is accessible simultaneously (Niimura *et al.*, 1982; Niimura, 1986). At present, area detectors are mainly used in combination with low-angle scattering techniques, but are also of growing interest for diffuse-scattering work (Arndt, 1986b).

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4.1

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