4. DIFFUSE SCATTERING AND RELATED TOPICS

last term in (4.2.5.91) describes space correlations. Omission of $\exp\{D_{l;\,l'}\}$ or expansion to $\sim(1 + D_{l;\,l'})$ are further simplifying approximations.

In either (4.2.5.88) or (4.2.5.91) 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.

(2) *Rotational structure (form) factor*

In certain cases and with simplifying assumptions, $\langle F \rangle$ [equation (4.2.5.87)] and $\langle \Delta F^2 \rangle$ [equation (4.2.5.90)] 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

$$\langle F \rangle = \sum_k f_k \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \qquad (4.2.5.92)$$

and

$$\langle \Delta F^2 \rangle = \sum_k \sum_{k'} f_k f_{k'} [\langle \exp\{2\pi i \mathbf{H} \cdot (\mathbf{r}_{lk} - \mathbf{r}_{l'k'})\} \rangle$$
$$- \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{lk}\} \rangle \langle \exp\{2\pi i \mathbf{H} \cdot \mathbf{r}_{l'k'}\} \rangle]. \qquad (4.2.5.93)$$

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

$$\langle F \rangle = \sum_k f_k j_0(\mathbf{H} \cdot \mathbf{r}_k) \qquad (4.2.5.94)$$

$$\langle |\Delta F|^2 \rangle = \sum_k \sum_{k'} f_k f_{k'} \{ j_0[\mathbf{H} \cdot (\mathbf{r}_k - \mathbf{r}_{k'})]$$
$$- j_0(\mathbf{H} \cdot \mathbf{r}_k) j_0(\mathbf{H} \cdot \mathbf{r}_{k'}) \}. \qquad (4.2.5.95)$$

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

In practice the molecules perform 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)].

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_{\mu=-\nu}^{+\nu} i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{(k)} Y_{\nu\mu}(\theta, \varphi). \qquad (4.2.5.96)$$

$j_\nu(z)$ is the νth order of spherical Bessel functions, the coefficients $C_{\nu\mu}^{(k)}$ characterize the angular distribution of $\mathbf{r}_k$ and $Y(\theta, \varphi)$ are the spherical harmonics where $|\mathbf{H}|$, θ, φ 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 $K_{\nu\mu}(\theta, \varphi)$:

$$\langle F \rangle = \sum_k f_k 4\pi \sum_\nu \sum_\mu i^\nu j_\nu(\mathbf{H} \cdot \mathbf{r}_k) C_{\nu\mu}^{'(k)} K_{\nu\mu}(\theta, \varphi), \qquad (4.2.5.97)$$

where $C_{\nu\mu}'$ are modified expansion coefficients.

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

$$\langle F' \rangle = \langle F \rangle \exp\{-\tfrac{1}{6} H^2 \langle U^2 \rangle\}. \qquad (4.2.5.98)$$

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)].

(3) *Short-range correlations*

The final terms in equations (4.2.5.88) and (4.2.5.91) concern correlations between the orientations of different molecules. Detailed evaluations need 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 4.2.3.5.1.

4.2.6. Disorder diffuse scattering from aperiodic crystals

The preceding sections of this chapter have either been related to disorder phenomena in conventional crystals defined by the presence of 3D translational symmetry, *i.e.* by a 3D lattice function, at least in the averaged sense, or to solids with crystalline order in only lower (2 or 1) dimensions where the ordering principle along 'nonperiodic' directions shows a gradual transition from long- to short-range order, in particular to a liquid-like behaviour and, finally, to an (almost) random ordering behaviour of structural units. So-called aperiodic crystals do not fit this treatment because aperiodicity denotes a different type of order, which is nonperiodic in 3D space but where translational order may be restored in higher-dimensional ($n > 3$) direct space. Three types of solids are commonly included in the class of aperiodic structures: (i) incommensurately modulated structures (IMSs), where structural parameters of any kind (coordinates, occupancies, orientations of extended molecules or subunits in a structure, atomic displacement parameters) deviate periodically from the average ('basic') structure and where the modulation period is incommensurate compared to that of the basic structure; (ii) composite structures (CSs), which consist of two (or more) intergrown incommensurate substructures with mutual interactions giving rise to mutual (incommensurate) modulations; and (iii) quasicrystals (QCs), which might simply be viewed as made up by n (≥ 2) different tiles – analogous to the elementary cell in crystals – which are arranged according to specific matching rules and which are decorated by atoms or atomic clusters. Most common are icosahedral (i-type) quasicrystals with 3D aperiodic order (3D 'tiles') and decagonal quasicrystals (d-phases) with 2D aperiodicity and one unique axis along which the QC is periodically ordered. The basic 'crystallography' of aperiodic crystals is given in Chapter 4.6 of this volume; see also the review articles by Janssen & Janner (1987) and van Smaalen (2004) (and further references therein). We only point out some of the aspects here to provide the background for a short discussion about disorder diffuse scattering in aperiodic crystals.

As outlined in Section 4.6.1, a d-dimensional (dD) ideal aperiodic crystal can be defined as a dD irrational section of an nD ('hyper'-)crystal with nD crystal symmetry. Corresponding to the section of the nD hypercrystal with the dD ($d = 1, 2, 3$) direct physical (= 'external' or 'parallel') space we have a projection of the (weighted) nD reciprocal hyperlattice onto the dD reciprocal physical space. The occurrence of Bragg reflections as a signature

of an ordered (in at least an averaged sense) aperiodic crystal form a countable dense pattern of the projected reciprocal (hyper-)lattice vectors. Disorder phenomena, *i.e.* deviations from the periodicity in higher-dimensional direct (hyper-)space, are thus related to diffuse phenomena in reciprocal (hyper-)space projected down to the reciprocal physical space. Therefore only fluctuations from the aperiodic order infer diffuse scattering in its true sense, which might be hard to discern in a dense pattern of discrete (Bragg) reflections. As a consequence, in the higher-dimensional description of aperiodic crystals the atoms must be replaced by 'hyperatoms' or 'atomic surfaces', which are extended along $(n - d)$ dimensions. If, for example, an IMS exhibits a modulation in only one direction (1D IMS), we have $n = 2$ and a 1D atomic surface (which is a continuous modulation function extended along the 1D 'internal' or 'perpendicular' subspace). The physical subspace is spanned by 1 (and +2 'unaffected') dimensions. In a second example, a decagonal QC with aperiodic order in two dimensions is described by $n = 4$ (plus the remaining coordinate along the unaffected periodic direction) and $d = 2$, *i.e.* by 2D atomic surfaces. The atomic surfaces are, as shown in Chapter 4.6, continuous n-dimensional objects for IMSs and CSs, and discrete ones in the case of QCs. In addition to the 'hyperlattice' fluctuations within the physical (parallel) subspace we have therefore an additional quality of disorder phenomena related to positions and shape and size fluctuations of the atomic surfaces within the perpendicular subspace. Therefore, one has to consider disordering effects in aperiodic crystals related to fluctuations in the (external) physical subspace as well as in the internal subspace, but one should bear in mind that the two types are often coupled. Disordering due to displacements along directions within the physical subspace are – in the context of aperiodic crystals – commonly termed 'phonon-like', in contrast to 'phason-like' disorder related to displacements parallel to directions within the internal subspace. The term phason originates from a particular type of (dynamical) fluctuations of an IMS (see below).

4.2.6.1. Incommensurately modulated structures

Quite generally, small domains with periodic or aperiodic structures give rise to broadening of reflections. Diffuse satellite scattering is due to the limited coherence length of a modulation wave within a crystal or due to short-range order of twin or nanodomains (with an 'internal' modulated structure) embedded in a periodic matrix structure. This type of diffuse scattering can be treated by the rules outlined in Section 4.2.3.5. Structural fluctuations with limited correlation lengths are, for example, responsible for diffuse scattering in 1D organic conductors (Pouget, 2004). In some cases, modulated structures are intermediate phases within a limited temperature range between a high- and low-temperature phase (*e.g.* quartz) where the structural change is driven by a dynamical instability (a soft mode). In addition to (inelastic) soft-mode diffuse scattering, dynamic fluctuations of phase and amplitude of the modulation wave give rise to diffuse intensity. In particular, the phase fluctuations, *phasons*, give rise to low-frequency scattering which might be observable as an additional diffuse contribution around condensing reflections.

4.2.6.2. Composite structures

In the case of CSs, diffuse scattering relates to interactions between the component substructures which are responsible for mutual modulations: each substructure becomes modulated with the period of the other. If one of the substructures is low-dimensional, for example chain-like structural elements embedded in tubes of a host structure, one observes diffuse planes if direct interchain correlations are mostly absent. The diffuse planes are, however, not only due to the included subsystem, but also due to corresponding modulations of the matrix structure. On the other hand, maxima superimposed on the diffuse planes reflect the influence of the matrix structure on the chain system. The thickness of the diffuse planes depends on the degree of short- or long-range order along the unique direction (*cf.* Section 4.2.5.3). This might be either a consequence of faults in the surrounding matrix which interrupt the (longitudinal) coherence of the chains (Rosshirt *et al.*, 1991) or, intrinsically, due to the degree of misfit between the periods of the mutually incommensurate structures of the host and guest structures. If this misfit becomes large, *e.g.* as a consequence of different thermal expansion coefficients of the two substructures, the modulation is only preserved within small domains and one observes a series of diffuse satellite planes (Weber *et al.*, 2000). Equivalent considerations relate to composite systems made up from stacks of planar molecules (*e.g.* van Smaalen *et al.*, 1998) or an intergrowth of layer-like substructures where the modulation is mainly due to a one-dimensional stacking along the normal to the layers. Correspondingly, quite extended diffuse streaks occur at positions of the satellites in reciprocal space.

A further discussion of the more complicated disorder diffuse scattering of higher- (than one-) dimensionally modulated IMSs and CSs and the corresponding diffuse patterns in reciprocal space is beyond the scope of this chapter. We refer to Section 4.6.3 and the references cited therein. For examples, see also Petricek *et al.* (1991).

4.2.6.3. Quasicrystals

As in the case of conventional crystals, there is no unique theory of diffuse scattering by quasicrystals. Chemical disorder, phonon- and phason-like displacive disorder, topological glass-like disorder and domain disorder exist. The term domain covers those with an aperiodic structure as well as periodic approximant domains, which are also known as approximant phases (*cf.* Section 4.6.3). Approximant phases exhibit local atomic clusters which do not differ significantly from those of related aperiodic QCs. In d-phases, disorder diffuse scattering occurs which is related to the periodic direction. Reviews of disorder diffuse scattering from quasicrystals are given, *e.g.*, by Steurer & Frey (1998) and Estermann & Steurer (1998).

Chemical disorder. Many of the quasicrystals are ternary intermetallic phases consisting of atomic clusters where two components are transition metals (TMs) with only a small difference in Z (the number of electrons). Most of them exhibit a certain amount of substitutional (chemical) disorder, in particular with respect to the distribution of the TMs. This behaviour is equally true in the approximant phases. Chemical short-range order between the TMs, if any, is largely uninvestigated because conventional X-ray diffraction and electron-microscopy methods are not sensitive enough to provide significant contrast between the TMs. If the X-ray form-factor difference Δf is small, X-ray patterns do not show diffuse scattering, whereas an analogous neutron pattern could reveal a diffuse component due to the different scattering contrast Δb of the TMs (where the b's are the neutron scattering lengths). In practice, the chemical disorder phenomena might be more complex as the compositional stability of the QCs is often rather extended and the atomic distribution in a sample is not always structurally homogeneous. Depending on the crystal-growth process, microstructures may occur with locally coexisting small QC domains with fluctuating chemical content and, moreover, coexisting QC and approximant domains. Chemical disorder might also be caused by phasonic disorder.

Phonon-type (static or dynamic) displacements, fluctuations or straining relate to the physical subspace coordinates giving rise to continuous local distortions of the atomic structure. Phason-type disorder describes, as indicated above, discontinuous atomic jumps between different sites in an aperiodic structure. Qualitatively, dominant phonon- or phason-related scattering may be separated by analysing the dependence of the diffracted inten-

sities on the components of the scattering vector in the external and the internal subspace, $H_e (Q_e)$ and $H_i (Q_i)$, respectively (*cf.* above and also Section 4.6.3). There are different kinds of phason-like disorder, including random phason fluctuations, phason-type modulations and phason straining, and also shape and size fluctuations of the hyperatomic surfaces. If displacing an atomic surface (hyperatom) parallel to an internal space component by any kind of phason fluctuation which is equivalent to an infinitesimal rotation of the external (physical) space, it might happen that the hyperatom no longer intersects the physical space. Then an empty site is created, which is compensated by a (real) atom 'appearing' at a different position in physical space. In addition, there might even be a change of atomic species as a hyperatom may be chemically different at different sites of the atomic surface. Randomly distributed phason strains are responsible for Bragg-peak broadening and Huang-type diffuse scattering close to Bragg peaks. There are well developed theories based on the elastic theory of icosahedral (*e.g.* Jaric & Nelson, 1988) or decagonal (Lei *et al.*, 1999) quasicrystals that also include phonon–phason coupling. An example of the quantitative analysis of diffuse scattering by an i-phase (Al–Pd–Mn) is given by de Boissieu *et al.* (1995) and by a d-phase (Al–Ni–Fe) by Weidner *et al.* (2004). Dislocations in quasicrystals have partly phonon- and partly phason-like character; a discussion of the specific dislocation-related diffuse scattering will not be given here (*cf.* Section 4.6.3). Arcs and rings of localized diffuse scattering are observed in various i-phases and could be modelled in terms of some short-range 'glass-like' ordering of icosahedral clusters (Goldman *et al.*, 1988; Gibbons & Kelton, 1993). Phason-related diffuse scattering phenomena are discussed in more detail in Section 4.6.3. Depending on the exact stoichiometry and the growth conditions, d-phases very often show intergrown domain structures where the internal atomic structure of an individual domain varies between a (periodic) approximant structure, more or less strained aperiodic domains, or transient aperiodic variants (Frey & Weidner, 2002). Apart from finite size effects of domains of any kind which cause peak broadening, there are complex diffraction patterns of satellite reflections, diffuse maxima and diffuse streaking in d-Al–Ni–Co and other d-phases (Weidner *et al.*, 2001). In various d-phases one also observes, in addition to the Bragg layers, prominent diffuse layers perpendicular to the unique 'periodic' axis. They correspond to n-fold ($n = 2, 4, 8$) superperiods along this direction. In different d-phases there is a gradual change from almost completely diffuse planes to layers of superstructure reflections (satellites). The picture of a kind of stacking disorder of aperiodic layers does not match such observations. An explanation is rather due to 1D columns of atomic icosahedral clusters along the unique direction (Steurer & Frey, 1998). The temperature behaviour of these diffuse layers was studied by *in situ* neutron diffraction (Frey & Weidner, 2003), which shed some light on the complicated order/disorder phase transitions in d-Al–Ni–Co.

4.2.7. Computer simulations and modelling

4.2.7.1. Introduction

The various analytical expressions given in Section 4.2.5 are mostly rather complex, so their application is often restricted to relatively simple systems. Even in these cases analytical solutions are often not available. For larger displacements the approximations that use an expansion of the exponentials [*e.g.* equation (4.2.3.27)] are no longer valid. Hence there is a need for alternative approaches to tackling more complicated disorder models. In the past, optical transforms (*e.g.* Harburn *et al.*, 1974, 1975) and the videographic method (Rahman, 1993) were developed for this purpose. In the first method, a 2D mask with holes with sizes that represent the scattering power of the atoms is gener-

ated, which is then subjected to coherent light (from a laser) to produce a diffraction image. Problems arise for strong scatterers requiring very large holes. These problems were overcome in the second method, where the mask is replaced by a computer image with intensities proportional to the scattering power for each pixel. With the advent of more and more powerful computers these methods are now replaced by complete computer simulations, both to set up the disorder model and to calculate the diffraction pattern.

4.2.7.2. Simulation programs

Having established a disordered crystal with the types and positions of all atoms involved (a configuration), *e.g.* by using one of the methods described below, computer programs employing fast-Fourier-transform techniques can be used to calculate the diffraction pattern, which may be compared with the observation. It has to be borne in mind, however, that there is still a large gap between a real crystal with its $\sim 10^{23}$ atoms and the one simulated by the computer with only several thousand atoms. This means that very long range correlations can not be included and have to be treated in an average manner. Furthermore, the limited size of the simulated crystal leads to termination effects, giving rise to considerable noise in the calculated diffraction pattern. Butler & Welberry (1992) have introduced a technique to avoid this problem in their program *DIFFUSE* by dividing the simulated crystal into smaller 'lots'. For each lot the intensity is calculated and then the intensities of all lots are summed up incoherently, which finally results in a smooth intensity distribution. Note, however, that in this case long-range correlations are restricted to even smaller values. To overcome this problem Boysen (1997) has proposed a method for suppressing the subsidiary maxima by multiplying the scattering density of the model crystal by a suitably designed weighting function simulating the effect of the instrumental resolution function.

A very versatile computer program, *DISCUS*, which allows not only the calculation of the scattering intensities but also allows the model structures to be built up in various ways, has been designed by Proffen & Neder (1999). It contains modules for reverse Monte Carlo (RMC, see below) simulation, the calculation of powder patterns, RMC-type refinement of pair-distribution functions (PDFs, see below) and many other useful tools for analysing disorder diffuse scattering.

Other computer programs have been developed to calculate diffuse scattering, some for specific tasks, such as *SERENA* (Micu & Smith, 1995), which uses a collection of atomic configurations calculated from a molecular dynamics simulation of molecular crystals.

4.2.7.3. Modelling procedures

Several well established methods can be used to create the simulated crystal on the computer. With such a crystal at hand, it is possible to calculate various thermodynamical properties and study the effect of specific parameters of the underlying model. By Fourier transformation, one obtains the diffraction pattern of the total scattering, *i.e.* the diffuse intensities and the Bragg peaks. The latter may lead to difficulties due to the termination effects mentioned in Section 4.2.7.2. These may be circumvented by excluding regions around the Bragg peaks (note, however, that in this case valuable information about the disorder may be lost), by subtracting the average structure or by using the approximation of Boysen (1997) mentioned above. A major advantage of such modelling procedures is that realistic physical models are introduced at the beginning, providing further insight into the pair interactions of the system, which can only be obtained *a posteriori* from the correlation parameters or fluctuation wave amplitudes derived from one of the methods described in Section 4.2.5.