

4. DIFFUSE SCATTERING AND RELATED TOPICS

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.

4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

4.2.7.3.1. Molecular dynamics

Molecular dynamics (MD) techniques have been developed to study the dynamics of a system. They may also be used to study static disorder problems (by taking time averages or snapshots), but they are particularly useful in the case of dynamic disorder, *e.g.* diffusing atoms in superionic conductors. The principle is to set up a certain configuration of atoms with assumed interatomic potentials $\Phi_{ij}(r_{ij})$ and subject them to Newton's equation of motion,

$$F_i(t) = m_i \frac{d^2 r_i(t)}{dt^2}, \quad (4.2.7.1)$$

where the force $F_i(t)$ is calculated from the gradient of Φ . The equations are solved approximately by replacing the differential dt by a small but finite time step Δt to find new positions $r_i(t + \Delta t)$. This is repeated until an equilibrium configuration is found. MD techniques are quite useful if only short-range interactions are effective, even allowing the transfer of potential parameters between different systems, but are less reliable in the presence of significant long-range interactions.

4.2.7.3.2. Monte Carlo calculations

Monte Carlo (MC) methods appear to be more suited to the study of static disorder and many examples of their application can be found in the literature. Different variants allowing simulations and refinements have been applied:

(1) *Direct MC simulation.* In this method, introduced by Metropolis *et al.* (1953), a starting configuration is again set up in accordance with the known average structure and other crystal, chemical and physical information if available, and an appropriate interaction potential is chosen. The choice of this potential can be a quite delicate task. On the one hand, it should be as simple as possible to allow as large a simulation box size as can reasonably be handled by the computer's capacity. On the other hand, it must be detailed enough to include all the relevant interaction parameters of the system. Frequently used interaction potentials are a pseudo spin Ising Hamiltonian, where the 'spins' can either be binary (*e.g.* atom types or molecular orientations) or continuous (displacements), and harmonic springs for the displacements.

Having set up the starting configuration and defined the Hamiltonian, one proceeds by choosing a specific site at random and changing its parameters (occupancies and positions) by a random amount (a 'move'). The energy of this new configuration is calculated and compared with the old one. If the difference ΔE is negative, the move is accepted. If it is positive it is accepted with a probability

$$P = \exp\{-\Delta E/k_B T\} / [1 + \exp\{-\Delta E/k_B T\}], \quad (4.2.7.2)$$

where T is a temperature and k_B is Boltzmann's constant. Then another site is chosen at random and the process is repeated again and again until an equilibrium configuration is found, *i.e.* until the energies fluctuate around some average value. After this, the corresponding intensity distribution is calculated and compared with the observed one. The parameters of the Hamiltonian may then be modified to improve the agreement between the calculated and observed diffraction patterns. This rather cumbersome trial-and-error method may be used to study the influence of the various parameters of the model. Further details of this method together with some illustrative examples may be found in Welberry & Butler (1994).

In an attempt to automate the adjustment of the model parameters, Welberry *et al.* (1998) have used a least-squares procedure to minimize

$$\chi^2 = \sum w(\Delta I)^2, \quad (4.2.7.3)$$

where ΔI are the differences between the observed and calculated intensities and w are the appropriate weights. The problem with this approach is that the necessary differentials $\delta\Delta I/\delta p_i$ must be calculated numerically by performing full MC simulations with parameters p_i and $p_i + \delta p_i$ at each iteration step, which presents a formidable task even for the fastest modern computers.

(2) *Reverse MC calculations.* Application of the direct MC method may be very time consuming, as many MC simulations are necessary to arrive at a final configuration. To overcome this problem, the so-called reverse Monte Carlo (RMC) method has been developed, originally for liquids and glasses (McGreevy & Pusztai, 1988) and later for disordered single crystals (Nield *et al.*, 1995).

RMC is a model-free approach, *i.e.* without the need to define a proper interaction Hamiltonian. Otherwise it proceeds in a very similar way to direct MC analysis. A starting configuration is set up and random 'moves' of the atoms are carried out. The only difference is that acceptance or non-acceptance of a move is based on the agreement between observed and calculated diffraction intensities, *i.e.* equation (4.2.7.2) is replaced by

$$P = \exp\{-\Delta\chi^2/2\}, \quad (4.2.7.4)$$

where χ^2 is defined in equation (4.2.7.3) and $\Delta\chi^2 = \chi_{\text{new}}^2 - \chi_{\text{old}}^2$. Usually only a single MC run is necessary to arrive at a configuration with a diffraction pattern consistent with the observation. A drawback of the RMC technique is that usually only one configuration is found satisfying the observed diffraction pattern. In fact, it is possible that different configurations may produce the same or very similar intensity distributions (see *e.g.* Welberry & Butler, 1994). In this context, it has to be borne in mind that the diffuse scattering contains information about two-body correlations only, while the physical reason for a particular disordered structure may also be influenced by three- and many-body correlations. Such many-body correlations can easily be incorporated in the direct MC method. Moreover, RMC is susceptible to fitting artefacts (noise) in the diffraction pattern. To avoid unreasonable atomic configurations, restrictions such as a limiting nearest-neighbour approach can be built in. Weak constraints, *e.g.* ranges of interatomic distances or bond angles (*i.e.* three-body correlations) can be introduced by adding further terms in the definition of χ^2 [equation (4.2.7.3)]. In the same way, multiple data sets (*e.g.* neutron and X-ray data, EXAFS measurements *etc.*) may be incorporated. For more details and critical reviews of this method see *e.g.* McGreevy (2001) and Welberry & Proffen (1998). Many applications of this method can be found in the literature, mainly for powder diffraction, but also for single-crystal data.

(3) *Simulated annealing and evolutionary algorithms.* A general problem with MC methods is that they may easily converge to some local minima without having found the global one. One way to reduce such risks is to start with a high probability in (4.2.7.2) by using a large 'temperature' T , *i.e.* initially allowing many 'false' moves before gradually reducing T during the course of the simulation cycles. This is called 'simulated annealing', although it has nothing to do with real annealing. In the RMC method one may introduce a weighting parameter similar to T in (4.2.7.2).

Another effective way to find the global minimum and also to accelerate the optimization of the energy parameters of a given MC model is by using the principles of evolutionary theory: selection, recombination and mutation. Two such evolutionary (or genetic) algorithms have been proposed: the differential evolution (DE) algorithm (Weber & Bürgi, 2002) and the cooperative evolution (CE) algorithm (Weber, 2005). A single parameter of the model is called a gene and a set of genes is called a chromosome, p being the genotype of an individual. First a population consisting of several individuals is built up and the corresponding diffraction patterns are calculated and compared

with the observation. The fitness of each individual is quantified by χ^2 . Children are then created by choosing one parent individual and calculating the second one from three randomly chosen individuals according to

$$p'_c = p_c + f_m(p_a - p_b), \quad (4.2.7.5)$$

where f_m governs the mutations. The chromosome of the child is obtained by combining the genes of the two parents governed by a crossover (or recombination) constant f_r . If its fitness is higher than that of the parent, it replaces it. This procedure is repeated until some convergence criterion is reached. This DE method is still rather time-consuming on the computer. Therefore, the CE technique was introduced, where only one crystal is built up during the refinement. Here a large population is created spanning a large but reasonable parameter space. Individuals are selected at random to decide upon acceptance or rejection of an MC move *via* their own energy criteria. Then χ^2 is calculated and according to its positive or negative change a gratification or penalty weight is given to that individual. It may live as long as this weight is positive, otherwise it is replaced by a new individual calculated from (4.2.7.5). This way, useful individuals live longer to act on the same crystal, while unsuccessful ones are eliminated early. Note that the recombination operation is not used in this technique.

(4) *The PDF method.* The pair-distribution function (PDF) has long been used for the analysis of liquids, glasses and amorphous substances (Warren, 1969), but has recently regained considerable interest for the analysis of crystalline substances as well (Egami, 1990; Billinge & Egami, 1993; Egami, 2004). The PDF is obtained by a Fourier transformation of the total (Bragg plus diffuse) scattering in a powder pattern,

$$\rho_0 G(r) = \rho_0 + \frac{1}{2} \int H[S(H) - 1] \sin(2\pi H) dH. \quad (4.2.7.6)$$

This is nothing other than the van Hove correlation function (4.2.2.2) or the related Patterson function (4.2.2.5) averaged spherically and taken at $t = 0$ (a snapshot) and is given by

$$G^{\text{PDF}}(r) = 4\pi r [\rho(r) - \rho_0] = \left(\sum c_i b_i \right)^{-2} 4\pi r \rho_0 G(r), \quad (4.2.7.7)$$

where ρ_0 is the average number density and

$$\rho(r) = (1/N) \sum (b_i b_j / \langle b \rangle^2) \delta(r - r_{ij}). \quad (4.2.7.8)$$

The δ functions are then convoluted with a normalized Gaussian to account for (harmonic) thermal motion. Parameter refinement proceeds in a similar way to the RMC technique. First a model is built, initially within just one unit cell and with periodic boundary conditions, then its PDF is calculated, compared with the observed one and further improved using, for example, MC simulated annealing. The model is then enlarged to include longer-range correlations. Owing to the small size of the models, this technique is much faster than the RMC method. It is essential, however, that data are measured up to very high H values to minimize truncation errors in (4.2.7.6).

4.2.7.3.3. General remarks

All of the different modelling techniques mentioned in this section have their specific merits and limitations and have contributed much to our understanding of disorder in crystalline materials following the interpretation of the corresponding diffuse scattering. It should be borne in mind, however, that application of these methods is still far from being routine work and it requires a lot of intuition to ensure that the final model is physically and chemically reasonable. In particular, it must always be ensured that the average structure remains consistent with that derived from the Bragg reflections alone. This may be done by keeping the Bragg reflections, *i.e.* by analysing the total

scattering, or by designing special algorithms, *e.g.* by swapping two atoms at the same time (Proffen & Welberry, 1997). Moreover, possible traps and corrections like local minima, termination errors, instrumental resolution, statistical noise, inelasticity *etc.* must be carefully considered. All this means that the analytical methods outlined in Section 4.2.5 keep their value and should be preferred wherever possible.

The newly emerging technique of using full quantum-mechanical *ab initio* calculations for structure predictions along with MD simulations may also be applied to disordered systems. The limited currently available computer power, however, restricts this possibility to rather simple systems and small simulation box sizes, but, with the expected further increase of computer capacities, this may open up new perspectives for the future.

4.2.8. Experimental techniques and data evaluation

Single-crystal and powder diffractometry are used in diffuse scattering work. Conventional and more sophisticated special techniques and instruments are now available at synchrotron facilities and modern neutron reactor and spallation sources. The full merit of the dedicated machines may be assessed by inspecting the corresponding handbooks, which are available upon request from the facilities. In the following, some common important aspects that should be considered when planning and performing a diffuse-scattering experiment are summarized and a short overview of the techniques is given. Methodological aspects of diffuse scattering at low angles, *i.e.* small-angle-scattering techniques, and high-resolution single-crystal diffractometers are excluded. Instruments of the latter type are used when diffuse intensities beneath Bragg reflections or reflection profiles and tails must be analysed to study long-range distortion fields around single defects or small defect aggregates. In the case of small defect concentrations, the crystal structure remains almost perfect and the dynamical theory of diffraction is more appropriate. This topic is beyond the scope of this chapter.

4.2.8.1. Single-crystal techniques

In general, diffuse scattering is weak in comparison with Bragg scattering, and is anisotropically and inhomogeneously distributed in reciprocal space. The origin may be a static phenomenon or a dynamic process, giving rise to elastic or inelastic (quasi-elastic) diffuse scattering, respectively. If the disorder problem relates to more than one structural element, different parts of the diffuse scattering may show different behaviour in reciprocal space and/or on an energy scale. Therefore, before starting an experiment, some principal aspects should be considered: Is there need for X-ray and/or neutron methods? What is the optimum wavelength or energy (band), or does a 'white' technique offer advantages? Can focusing techniques be used without too strong a loss of resolution and what are the best scanning procedures? How can the background be minimized? Has the detector a low intrinsic noise and a high dynamic range?

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. Several sections through reciprocal space help to define the problem. For this purpose 'old-fashioned' film methods may be used, where the classical film is now commonly replaced by an imaging plate (IP) or a charge-coupled device (CCD) camera (see below). Clearly, short crystal-to-detector distances provide larger sections and avoid long exposure times, but suffer from spatial resolution. Distorted sections through the reciprocal lattice, such as produced by the Weissenberg method, may be transformed into a form suitable for easy interpretation (Welberry, 1983). The transformation of diffuse data measured using an IP or CCD requires suitable