4. DIFFUSE SCATTERING AND RELATED TOPICS

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

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

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,

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

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

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

where ρ_0 is the average number density and

$$\rho(r) = (1/N) \sum (b_i b_{i'}/\langle b \rangle^2) \delta(r - r_{ii'}). \qquad (4.2.7.8)$$

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

references