2.4. ELECTRON POWDER DIFFRACTION

diffraction data of nanocrystalline materials are encouraging. The refinement for powders containing large crystal grains is problematic because of dynamical scattering present in the data. There are also uncertainties caused by instrumental effects. The dynamical effects can be accounted for using the Blackman formalism, while the influence of diverse instrumental parameters needs further systematic study.

2.4.7. The pair distribution function from electron diffraction data

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An extensive description of pair distribution function (PDF) analysis covering data acquisition, reduction and interpretation can be found in Chapter 5.7. Here, only a short outline is presented, concentrating on aspects that are specific to PDFs obtained by electron diffraction.

Poorly crystalline and amorphous materials exhibit no long-range order and therefore show no pronounced Bragg peaks in diffraction patterns. Nevertheless, owing to defined bonding geometry, these materials do have a specific local arrangement of atoms, denoted as short-range order. The short-range order can be analysed using the PDF obtained from the total scattering profile. The PDF can provide general information about the degree of order, the character of local atomic packing and the size of the correlation domains. The total scattering function is collected over a wide range of reciprocal space and includes not only the Bragg reflections (if present), but also the diffuse scattering information between them (Egami & Billinge, 2003).

The PDF $G(r)$ represents the probability of finding a pair of atoms with an interatomic distance r, weighted by the scattering power of the individual atoms. After normalization and suitable corrections, the reduced scattering function $F(Q)$ is derived. [In the PDF analysis, the scattering vector Q, which is related to the scattering angle θ as $Q = (4\pi \sin \theta)/\lambda$ is used, instead of $S = \sin \theta/\lambda$.] The PDF can be calculated by the Fourier transformation of $F(Q)$ into direct space (Warren, 1990; Egami & Billinge, 2003; Farrow & Billinge, 2009).

Powder diffraction data for PDF analysis should be measured over a sufficiently large range of the scattering angle θ; therefore, neutron or synchrotron sources or laboratory X-ray data with a short-wavelength source (Mo or Ag anode) are used. Powder electron diffraction data, with their flexibility in electron diffraction camera length, short wavelength and nuclear scattering at large scattering angles, can also cover the desired large range of scattering angles and are therefore highly suitable for PDF analysis. In addition, atoms have a much larger scattering cross section for electrons than for X-rays or neutrons, allowing sufficient signal collection from very small volumes. Finally, electrons can be focused with lenses down to a few nanometres. All these reasons make electron diffraction analysis attractive for the study of the structure of nanovolumes. The electron PDF is therefore a powerful tool for the investigation of the structures of amorphous or poorly crystalline thin films, or for small sample volumes of inhomogeneous samples.

There are several practical issues to consider when collecting electron diffraction data for PDF analysis:

Energy filtering. Traditionally, electron diffraction data for PDF analysis are collected using energy filtering in order to exclude the inelastic scattering contribution. However, quantitative or semi-quantitative electron PDFs can be obtained without filtering (Abeykoon *et al.*, 2012).

Multiple scattering/dynamical effects. In order to keep the contribution of non-kinematic scattering low, the sample thickness and the nanoparticle size should be as small as possible. Generally, particles 10 nm and smaller should scatter kinematically, and this is the size range that benefits most from PDF analysis (Abeykoon *et al.*, 2012).

Powder average. Proper statistics are important for PDF analysis. In order to decrease measurement errors one can increase the illumination area on the sample (or the selected-area aperture in the case of SAED), collect several diffraction patterns from different areas and average them.

Scattering angle range. A large θ range is essential for PDF analysis. An electron diffraction experiment offers significant flexibility in selecting the scattering range through the adjustment of the electron diffraction camera length and illumination wavelengths. Additionally, in order to enhance the data quality, merging of different scattering ranges recorded in a set of diffraction patterns is possible (Petersen *et al.*, 2005).

An electron diffraction pattern is a combination of signals produced by *elastically* and *inelastically* scattered electrons. The inelastic component is a result of electron energy loss due to plasmon or inner-shell excitation, electron Compton or thermal diffuse scattering (Egerton, 2011). For crystalline materials with distinct Bragg peaks the inelastic scattering is not particularly critical, as it mainly contributes to the background in diffraction patterns and can be neglected when only the intensities of the Bragg peaks are analysed. For PDF analysis the total scattering profile is used; thus, the inelastic scattering, which can significantly modify the scattering profile, needs to be considered (Ishimaru, 2006). Two strategies are followed in this respect: (i) energy filtering of diffraction patterns, which is the more accurate approach but demands specific instrumentation, and (ii) subtraction of the background scattering taken from an area adjacent to the sample (*i.e.* from the supporting film), which assumes that the main inelastic scattering component originates from the support, and the contribution from the sample can be neglected (Cockayne, 2007). The validity of this approximation depends on the level of quantification intended in the particular study.

The PDF formalism presented above is based on the single-scattering approximation. Multiple scattering, which is much stronger in electron diffraction than for X-rays and neutrons, significantly affects the total scattering profile and therefore the PDF. The multiple-scattering effects can modify the peak positions in the PDF as well as the relative intensities of the peaks, the latter being more sensitive to multiple scattering (Anstis *et al.*, 1988). It has been shown that for amorphous materials, owing to the contribution of the multiple scattering, the total scattering profile depends on the thickness of the foil (Childs & Misell, 1972; Rez, 1983). Knowledge of the film thickness allows extraction of the single-scattering distribution. An improved agreement with the expected PDF was shown for hydrogenated amorphous silicon (Anstis *et al.*, 1988) and amorphous germanium (Ankele *et al.*, 2005) using the single-scattering profile.

Experimentally, it is difficult to determine the sample thickness along the incident-electron-beam direction. In this case, the thickness parameter employed in calculations can be varied, adjusting the amplitudes of the PDF. An estimate for the sample thickness is found when the optimal fit is obtained. Different input values of the thickness result in different principal gradients of the oscillations. Once a reasonable fit is found, the correct thickness is determined and the contribution of multiple scattering can be eliminated (Ankele *et al.*, 2005). This method was

applied to amorphous NiNb alloy, allowing an estimate of the foil thickness, and thereafter improved the fit to the PDF obtained from Ag-anode X-ray scattering experiments (Ankele *et al.*, 2005).

Alternatively, the wavelength dependence of the multiple-scattering term can be used. A set of diffraction patterns of a glassy carbon film was collected from the same sample (apparently having the same thickness) using different wavelengths (Petersen *et al.*, 2005). These patterns were then processed in order to retrieve the single-scattering profile of tetrahedral amorphous carbon, which showed an improved fit to the reduced scattering function obtained with neutrons (Petersen *et al.*, 2005). This method can be applied to materials for which significant multiple scattering is expected and the thickness of the foil cannot be determined *a priori*. For very thin films the contribution of the multiple scattering is very low and, therefore, often neglected.

The PDF of elemental materials arising from only one contributing atomic scattering function can be directly interpreted in terms of coordination numbers and allows conclusions to be drawn about the local structure. PDF analysis of amorphous silicon prepared by deposition showed the existence of voids in the structure (Moss & Graczyk, 1969) which anneal on progressive heating. PDF investigation of amorphous carbon films prepared by arc plasma deposition showed that the material mainly consists of tetrahedrally coordinated carbon rather than having a graphitic structure (McKenzie *et al.*, 1991).

For ZrNi and ZrCu metallic glasses, partial PDFs were obtained by reverse Monte Carlo simulation (McGreevy & Pusztai, 1988) and fitted to the experimentally obtained electron scattering data. The analysis of the polyhedral statistics showed that the average coordination number of Cu was 11, while for Ni it was less than 10 (Hirata *et al.*, 2007). Study of amorphous FeB alloys (Hirata *et al.*, 2006) and $Fe_{90}Zr_7B_3$ (Hirotsu *et al.*, 2003) by PDF analysis allowed detection of nanoscale phase separation resulting in the formation of a mixture of different clusters.

Nanocrystals can be efficiently analysed by electron PDF analysis, giving information complementary to TEM imaging. The electron PDF of detonation nanodiamonds (DND) was used to estimate the average domain size (Zhang, 2011). Studies of phase separation in AgCu alloys showed the complex behaviour of the material with variation of temperature (Chen & Zuo, 2007). In the first stage, the nanodomains of the two terminal phases (Ag- and Cu-rich) are built; in the second stage, de-wetting of the thin film and formation of large Ag and Cu grains occur. A comparison of electron PDFs from nanocrystalline, partially ordered and amorphous parts of silica glasses (Kovács Kis *et al.*, 2006) allowed the estimation of the degree of order developed by changing the connectivity and orientation of the undistorted SiO_4 tetrahedra. Indirect detection of hydrogen atoms was performed from a modified distribution of atomic distances in soot samples using electron PDF analysis (Kis *et al.*, 2006).

With an increase in the particle size the deviations from the kinematical scattering become severe. Nevertheless, the electron PDF calculated for 100 nm Au crystals reproduced the simulated data quite well: the peak positions and relative amplitudes were not significantly modified (Abeykoon *et al.*, 2012).

2.4.8. Summary

Powder electron diffraction can be used for materials structural characterization, just as is routinely done using X-rays and neutrons. The specific characteristics of electron scattering result in both benefits and drawbacks to using electron diffraction data. Strong scattering of electrons allows collection of a sufficient signal from nanovolumes of material, thus offering the possibility of studying small amounts of material and thin films. The opportunity to couple the diffraction information with imaging gives the unique possibility of performing a structural study on the nanoscale in a controlled way. The strong interaction of electrons with matter leads to dynamical-scattering effects that result in deviation of the electron diffraction intensities from the kinematical model. Since the amount of the dynamical-scattering component in a powder sample is difficult to quantify, the quantitative use of electron diffraction intensity data is limited. For large crystals, the dynamical treatment of electron diffraction data is efficiently done in CBED analysis, providing exclusive information about the structure. For nanocrystalline or amorphous materials, an increasing number of sets of experimental data show that quantitative structure information can be obtained using electron powder diffraction. This encourages further applications of different kinds of electron diffraction data, giving new perspectives for the quantitative use of electron diffraction in general.

APPENDIX A2.4.1
Computer programs for electron powder diffraction

CHECKCELL is a graphical powder-pattern indexing helper and space-group-assignment program that links into the *CRYS-FIRE* powder indexing suite. More information and the program are available at http://www.ccp14.ac.uk/tutorial/lmgp/achekcelld.htm.

CRYSFIRE is a powder-pattern indexing system for DOS/Windows for unit-cell parameter determination from powder data (free for academic use). More information and the program are available at http://www.ccp14.ac.uk/tutorial/crys/.

ELD is a commercial program for calibrating and integrating two-dimensional electron diffraction patterns. The program is commercially available from Calidris, Sweden. More information is available from http://www.calidris-em.com/eld.php.

Electron diffraction pattern atlas. The website of Professor Jean-Paul Morniroli (http://electron-diffraction.fr/) provides an atlas of electron diffraction patterns that can be used to identify the space group of a crystal from observation of a few typical PED and CBED zone-axis patterns.

FIT2D is a general-purpose image and diffraction processing program, designed for use with synchrotron data, that integrates pre-selected sections of either one-dimensional or two-dimensional data. Corrections for geometrical distortion and for nonlinearity of intensity are included. It is available both for the Windows operating system (and DOS window) and for Macintosh OSX. The program is freely available for academic users. More information and the program are available at http://www.esrf.eu/computing/scientific/FIT2D/.

JEMS is a popular suite of simulation routines for a variety of platforms, mainly used for simulating high-resolution TEM (HRTEM), CBED, PED and SAED patterns. Simulation of powder diffraction rings is also included. The student version is free of charge. A licence is available from the author: http://www.jems-saas.ch/.

PCED is a program for the simulation of polycrystalline electron diffraction patterns (Li, 2010). A licence file is needed to unlock the program for loading input data files. More information is available at http://www.unl.edu/ncmn-cfem/xzli/.

references