2. INSTRUMENTATION AND SAMPLE PREPARATION

Atomic displacement parameters can be refined from electron powder diffraction data; however, the interpretation of the results can be manifold. For nanocrystalline materials, which have a relatively high surface-to-volume ratio, the surface effect can be enhanced compared with that of the bulk. Thus, the average atomic displacement factors can increase because of the high fraction of near-surface relaxed atoms. Consequently, the isotropic displacement parameter B resulting from the Rietveld refinement can be relatively high. Local heating (Reimer, 1984) during the electron illumination may also contribute to higher average displacement parameters. Finally, if the electron beam exceeds a material-dependent threshold acceleration voltage, it can cause knock-on damage (Williams & Carter, 2009) in both organic and inorganic materials. This is a dynamical process which can cause both material loss and rearrangement of atoms. The presence of defects resulting from the rearrangement of atoms may lead to an increase in the average displacement factors. Nevertheless, the refinement using polycrystalline anatase data showed the expected displacement parameters of 1.4 (1) Å^2 for Ti and 1.9 (2) Å^2 for oxygen (Weirich *et al.*, 2000). Of all the parameters used during Rietveld refinement, the displacement parameters and atomic coordinates are probably the most sensitive to a possible dynamical-scattering contribution in the data. It is noticeable that after the refinement of the anatase structure the atomic coordinates converged to reasonable positions: $[0, \frac{1}{4}, 0.1656\,(5)]$ for oxygen (Weirich *et al.*, 2000) compared with the previous range obtained in neutron diffraction studies of $[0, \frac{1}{4}, 0.16686\,(5)]$ (Burdett *et al.*, 1987) to $[0, \frac{1}{4}, 0.20806\,(5)]$ (Howard *et al.*, 1991).

The relative ratio of two components in a mixture can be determined using the Hill–Howard approach (Hill & Howard, 1987): the relative weight of a phase in a mixture of phases is proportional to the scaling factor of the phase given by the Rietveld refinement combined with the mass and the volume of the unit cell of the component. The relative content of a mixture of anatase and brookite was successfully determined from electron powder diffraction data (Djerdj & Tonejc, 2005, 2006).

For the modelling of the Bragg reflection shape the Pearson VII function can be used (Weirich *et al.*, 2000; Kim *et al.*, 2009), although recently the more popular pseudo-Voigt peak shape function has been used (Tonejc *et al.*, 2002; Djerdj & Tonejc, 2005, 2006) and provides a satisfactory fit between the experimental and calculated data.

The average crystalline domain size can be determined using line-broadening analysis. The measured intensity profile is a convolution of the physical line profile given by the sample with the instrumental profile broadening. When expressed in terms of the scattering angle θ, the width of the electron diffraction peaks is much smaller than that for X-rays. On the other hand, electrons generally have a smaller coherence length than X-rays. As a result, for the same material, the effective peak width for electron diffraction is larger than that for powder X-ray data (Song *et al.*, 2012). Because of this, it is sometimes difficult to separate the domain size and the instrumental contributions to the peak broadening. Therefore, the average domain size obtained after the refinement procedure should be cross-checked with the domain size determined from TEM images obtained, for instance, using the dark-field technique (Williams & Carter, 2009).

In electron diffraction various instrumental parameters can affect the peak width. The energy spread of the electrons causes additional broadening of diffracted spots. This effect can be partially reduced by energy filtering of the diffraction patterns (Kim *et al.*, 2009; Egerton, 2011). Finally, the electron diffraction
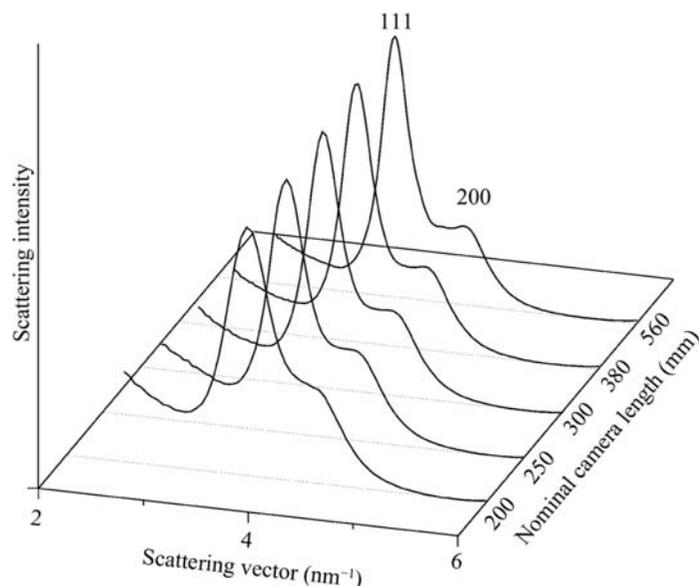

Figure 2.4.9
Electron powder diffraction profiles of gold nanoparticles (range 2–6 nm^{-1}) recorded at different electron diffraction camera lengths.

camera length must be large enough that the detector broadening is much smaller than the peak width, as demonstrated in Fig. 2.4.9: large values of the camera length ('zoomed in' diffraction patterns) result in thinner, better separated peaks.

Preferred orientation can be an issue for electron powder diffraction: when the powder material is supported on a thin film, the crystals tend to orient themselves with their most developed facet facing the support. As a result, the relative intensities of the diffracted peaks are modified (Kim *et al.*, 2009). Texture within nanocrystalline powders introduced by the sample preparation on a support for TEM can be analysed using electron powder diffraction patterns recorded at different tilt positions of the sample. Refinement of the preferred orientation of two different materials – nanocrystalline aluminium and α-MnS powders – showed that the aluminium particles tend to have strong preferred orientation due to their facet morphology, while α-MnS particles are randomly oriented (Gemmi, Fischer *et al.*, 2011).

Although dynamical effects are believed to be reduced for nanocrystalline materials and additionally reduced by data collection from non-oriented crystals, the dynamical component of the scattering cannot be neglected. For the dynamical correction using the two-beam approximation formalism of equation (2.4.12), the reader is referred to Section 2.4.2. For a range of electron-beam energies from 20 to 50 kV it has been shown that polycrystalline electron diffraction patterns of aluminium crystals smaller than 9 nm have a dynamical scattering component below 10% (Horstmann & Meyer, 1962). For polycrystalline $MnFe_2O_4$ with an average crystal size of 11 nm measured using a 120 kV electron beam, the ratio of the kinematical to dynamical contributions in the structure factor was about 1:1.5 (Kim *et al.*, 2009). The application of the small (less than 3%) correction for the dynamical component during Rietveld refinement of nanocrystalline intermetallic Au_3Fe_{1-x} improved the refined long-range order parameter of the alloy (Luo *et al.*, 2011).

In summary, the Rietveld refinement technique applied to electron powder diffraction data is a new area of research. It can be successfully carried out for small volumes of nanocrystalline materials, for which the small electron beam is an advantage. Results obtained from Rietveld analysis of electron powder

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