ODF were obtained for both sediment aggregates and evaporated thin films (Gemmi, Voltolini *et al.*, 2011).

2.4.6. Rietveld refinement with electron diffraction data

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The Rietveld refinement method was initially developed for neutron diffraction data (Rietveld, 1967, 1969). It has now become a standard technique which is extensively used with neutron, laboratory X-ray and synchrotron diffraction data. A detailed description of the method can be found in Chapter 4.7.

Compared with the popularity of Rietveld refinement in X-ray and neutron powder diffraction, its application to powder electron diffraction data is very limited. So far, Rietveld refinement with electron diffraction data has only been done for nanocrystalline Al, α-MnS (Gemmi, Fischer *et al.*, 2011), hydroxyapatite (Song *et al.*, 2012), intermetallic AuFe (Luo *et al.*, 2011), TiO_2 (Weirich *et al.*, 2000; Tonejc *et al.*, 2002; Djerdj & Tonejc, 2005, 2006) and $MnFe_2O_4$ (Kim *et al.*, 2009). An example of a fit with powder electron diffraction data obtained by Rietveld refinement for hydroxyapatite is shown in Fig. 2.4.7.

Two major factors limit the application of Rietveld refinement to electron powder diffraction. First, electron powder diffraction data are collected from a sample volume far smaller than that used in an X-ray experiment. Therefore, the average statistics are poor compared with those of X-ray data. Nevertheless, electron powder diffraction data from a small sample area or thin films can give specific information which is difficult to obtain using other methods. Second, the presence of dynamical effects in the electron diffraction data hinders quantitative assessment of reflection intensities. Dynamical effects are strongest in zone-axis electron diffraction geometry, when many beams belonging to the same systematic rows are excited simultaneously. In powder electron diffraction crystals are randomly oriented towards the electron beam, thus making the fraction of zonal patterns low, thereby reducing the dynamical scattering in the data (see Section 2.4.2 for a more detailed discussion).

Within the limit of kinematical diffraction, the principle of Rietveld refinement is the same for electrons and X-rays, except the electron atomic scattering factors are different. The refinement procedure can thus be performed using existing programs if it is possible to input the scattering factors for electrons. Most of the reported Rietveld refinements on electron powder diffraction data have been performed using *FullProf* (Rodríguez-Carvajal, 1993); a refinement in *MAUD* (Lutterotti *et al.*, 1999) has also been reported (Gemmi, Voltolini *et al.*, 2011).

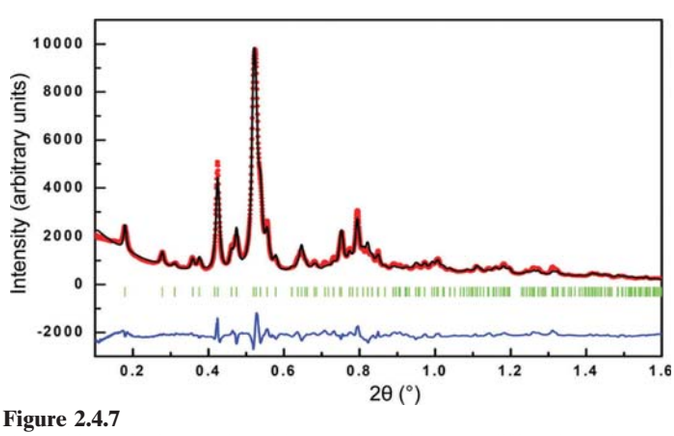

Figure 2.4.7
Rietveld analysis result with powder electron diffraction data of hydroxyapatite. Reproduced from Song *et al.* (2012) with permission from Oxford University Press.

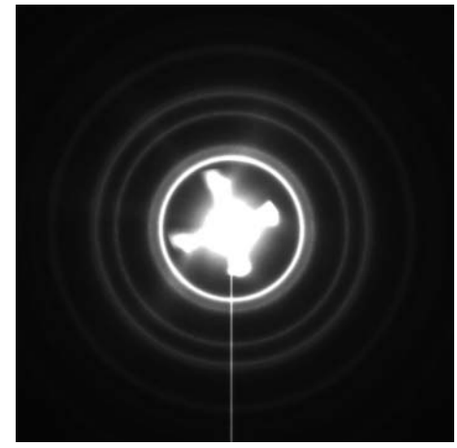

Figure 2.4.8
Powder electron diffraction pattern of nanocrystalline gold demonstrating non-symmetrical background features.

Electron powder diffraction patterns are recorded on an area detector. For a Rietveld refinement the two-dimensional diffraction patterns have to be integrated into one-dimensional profiles. The zero shift is treated as for the X-ray data integrated from a two-dimensional position-sensitive detector. Details about electron diffraction data processing and calibration are given in Section 2.4.3.4.

The background in electron powder patterns is a complex combination of inelastic scattering, scattering from the supporting film (when it is present) and other factors. For the Rietveld refinement procedure the background of a one-dimensional integrated profile is fitted by a polynomial function. If a supporting thin amorphous carbon film is used, the background can include broad rings, which after the one-dimensional integration can produce pronounced broad peaks. These peaks are difficult to subtract using a model based on a polynomial function; therefore, these intensities may hamper the powder diffraction profile matching (Kim *et al.*, 2009). In some cases, the background can even include radially non-symmetric features originating from the shape of the tip within the electron source (see Fig. 2.4.8); it can have blooming due to oversaturated CCD pixels, or streak shadows due to the fast transmission electron microscope beam-shutter movement. In these cases, a diffraction pattern from the adjacent 'empty' area of the sample can be acquired and subtracted from the diffraction pattern of the material prior to the integration into one dimension. This procedure allows elimination of some of the artifacts discussed above, which otherwise after the one-dimensional integration may be falsely interpreted as diffraction peaks, and are generally more difficult to fit.

Unit-cell parameters are mostly subject to the error due to the accuracy of the electron diffraction camera-length calibration. Although examples have been published showing 0.3% accuracy of the camera-length calibration, in most cases accuracy of about 2% can be achieved (Williams & Carter, 2009). The effective camera length depends on many instrumental parameters such as the convergence of the electron beam, the diffraction lens focus, the mechanical position of the sample within the objective lens, or the hysteresis of the electromagnetic lenses. Thus, while the ratio of the lattice parameters within one aligned diffraction pattern can be very precise, the absolute values might not be.

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