

## 2.4. Electron powder diffraction

J.-M. ZUO, J. L. LÁBÁR, J. ZHANG, T. E. GORELIK AND U. KOLB

### 2.4.1. Introduction

Electron powder diffraction is commonly performed in transmission geometry inside a transmission electron microscope using  $\sim 80\text{--}300$  kV high-energy electrons with wavelengths from 0.0418 to 0.0197 Å (Cowley, 1992; Peng *et al.*, 2004). The incident electron beam can be as small as a few nm or as large as tens of  $\mu\text{m}$  in diameter. Transmission electron powder diffraction can be obtained from randomly oriented nanocrystalline or amorphous materials. The short electron wavelengths allow the observation of powder diffraction rings over a large range of  $S$  ( $= \sin \theta / \lambda$ ). Electron powder diffraction can also be performed using the Bragg reflection geometry in reflection high-energy electron diffraction (RHEED) with 10–30 kV electrons (Ichimiya & Cohen, 2004). RHEED has a limited penetration depth and therefore is mostly used for the study of supported nanoparticles.

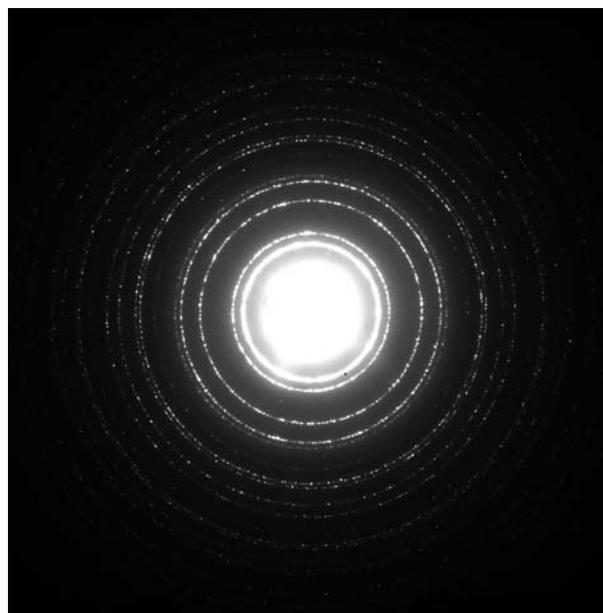
Because the electron beam can be formed into a small probe using electromagnetic lenses in a transmission electron microscope, electron diffraction has the advantage of being able to address individual particles in a powder as single crystals. Single-crystal electron diffraction data are often used for the determination of unit-cell parameters (Zuo, 1993; Zuo *et al.*, 1998; Gramm *et al.*, 2006; Sun *et al.*, 2009; Kolb *et al.*, 2006; Zhuang *et al.*, 2011), phase identification (Gramm *et al.*, 2006) or quantitative structural analysis (Vincent & Exelby, 1991; Jansen *et al.*, 1998; Tsuda & Tanaka, 1999; Hovmoller *et al.*, 2002; Sun *et al.*, 2009; Gorelik *et al.*, 2010; Mugnaioli *et al.*, 2012), or in combination with X-ray and neutron powder diffraction for structure determination (Wu *et al.*, 2006; Baerlocher *et al.*, 2007; McCusker & Baerlocher, 2009).

The principle of electron diffraction is similar to that of X-ray diffraction. Both use atomic scattering and interference of the scattered waves to probe the atomic structure. The difference is that electrons are charged particles and interact with both the electrons and nucleus of the atom with a large elastic scattering cross section (several orders of magnitude larger than that of X-rays). The combination of short wavelength, the large scattering cross section and the small electron beam makes electron powder diffraction a powerful technique for the analysis of amorphous or nanocrystalline thin films, nanoparticles and 'small' crystals in general (see Fig. 2.4.1 for an example).

A drawback of the strong interaction of electrons with matter is the presence of multiple-scattering effects. In X-ray diffraction, the measured integrated intensity is often less than predicted by the theory for an ideally imperfect crystal (because of extinction) but larger than predicted by the theory for an ideal perfect crystal. There are two types of extinction: primary and secondary. Primary extinction describes the multiple scattering within a single mosaic block. Primary extinction diminishes the intensity when the mosaic blocks are so large that they behave as fragments of perfect crystals. The effect of electron multiple scattering is similar to primary extinction in X-ray diffraction, except the electron extinction length is short and comparable with the sample thickness. Strong extinction can be an issue when analysis based on kinematical diffraction (single-scattering) theory, as in X-ray powder diffraction, is used for electron diffraction inten-

sities; thus dynamic theory, which takes into account multiple scattering of the incident and diffracted waves inside a crystal, is necessary. Secondary extinction also occurs in electron powder diffraction. However, so far there is no satisfactory treatment of this effect in electron diffraction. For small nanoparticles or nanocrystalline thin films the electron multiple-scattering effects are typically reduced, so quantitative structural information can be extracted from electron powder diffraction using the kinematical approximation (Cockayne & McKenzie, 1988; Ishimaru *et al.*, 2002; Chen & Zuo, 2007; Cockayne, 2007). Recent studies have demonstrated that multiple-scattering effects can be significantly reduced by averaging over a range of crystal orientations using precession electron diffraction (Vincent & Midgley, 1994; Gjonnes *et al.*, 1998; Gemmi *et al.*, 2003; Own *et al.*, 2006; Oleynikov & Hovmoller, 2007). The same benefit is expected in electron powder diffraction with 360° orientation averaging.

The quality of electron powder diffraction work has also benefited from the development of TEM (transmission electron microscopy) technologies. The adoption of field emission guns (FEGs) in conventional transmission electron microscopes led to the development of electron sources with high brightness, small probe size and improved coherence. Electron energy filters, such as the in-column  $\Omega$  energy filter, allow a reduction of the inelastic background due to plasmon scattering, or higher electron energy losses, with an energy resolution of a few eV (Rose & Krahl, 1995). The development of array detectors, such as charge-coupled device (CCD) cameras or image plates, enables the recording of entire powder diffraction patterns and direct quantification of diffraction intensities over a large dynamic range that was not possible earlier (Zuo, 2000). The latest



**Figure 2.4.1**

An electron powder diffraction pattern recorded on an imaging plate from a polycrystalline Al thin film using selected-area electron diffraction geometry with 200 kV electrons.