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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, dewetting 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 *CRYSFIRE* 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/.

PDFgui and *PDFfit2* are programs for full-profile fitting of the atomic PDF derived from X-ray or neutron diffraction data. *PDFgui* is a graphical front end for the *PDFfit2* refinement program, with built-in graphical and structure-visualization capabilities. *PDFgui* is currently in beta release and it is distributed as part of the DiffPy library. More information and the program are available at http://www.diffpy.org.

Process Diffraction is designed for processing of SAED and NAED patterns. It includes quantitative determination of phase fractions and texture from ring patterns recorded from nanocrystalline thin films in TEM. More information and the program are available at http://www.energia.mta.hu/~labar/ProcDif.htm.

QPCED and *PCED* are Java-based software for digitization, processing, quantification and simulation of powder electron diffraction patterns. For information contact Dr X. Z. Li (xzli@unl.edu) or visit http://www.unl.edu/ncmn-cfem/xzli.

TexPat is a program for quantification of texture (preferred orientation) from a tilt series of ring patterns recorded from nanocrystalline thin films in TEM (Oleynikov & Hovmoller, 2004).

WebEMAPS is a suite of computer programs that can be obtained at http://cbed.matse.illinois.edu/software_emaps.html. The programs include functions for visualization of crystal structures, simulation of single-crystal diffraction patterns, dynamic electron diffraction simulation, and calculations of electron structure factors and lattice *d*-spacings.

WinPLOTR is a peak-search program for plotting powder diffraction patterns and can be used as a graphical user interface for several programs used frequently in powder diffraction data analysis (*e.g. FullProf*, *DicVOL*, *SuperCELL*). *WinPLOTR* has been developed to run on PCs with a 32-bit Microsoft Windows operating system. More information and the program are available at http://www.cdifx.univ-rennes1.fr/winplotr/readme.htm.

References

Abeykoon, M. C. D., Malliakas, C. D., Juhás, P., Bozin, E. S., Kanatzidis, M. G. & Billinge, S. J. L. (2012). *Quantitative nanostructure characterization using atomic pair distribution functions obtained from laboratory electron microscopes. Z. Kristallogr.* **227**, 248–256.

Ankele, J., Mayer, J., Lamparter, P. & Steeb, S. (2005). *Quantitative electron diffraction data of amorphous materials. Z. Naturforsch. A*, **60**, 459–468.

Anstis, G. R. Z., Liu, Z. & Lake, M. (1988). *Investigation of amorphous materials by electron diffraction – the effects of multiple scattering. Ultramicroscopy*, **26**, 65–69.

Baerlocher, C., Gramm, F., Massüger, L., McCusker, L. B., He, Z., Hovmöller, S. & Zou, X. (2007). *Structure of the polycrystalline zeolite catalyst IM-5 solved by enhanced charge flipping. Science*, **315**, 1113–1116.

Barna, Á. & Pécz, B. (1997). *Preparation techniques for transmission electron microscopy.* In *Handbook of Microscopy*, edited by S. Amelinckx, D. van Dyck, J. van Landuyt & G. van Tendeloo, Vol. 3, pp. 751–801. Weinheim: Wiley-VCH Verlag GmbH.

Blackman, M. (1939). *On the intensities of electron diffraction rings. Proc. R. Soc. London Ser. A*, **173**, 68–82.

Botton, G. (2007). *Analytical electron microscopy.* In *Science of Microscopy*, edited by P. Hawkes & J. C. H. Spence, pp. 273–405. New York: Springer.

Burdett, J. K. T., Hughbanks, T., Miller, G. J., Richardson, J. W. & Smith, J. V. (1987). *Structural–electronic relationships in inorganic solids: powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K. J. Am. Chem. Soc.* **109**, 3639–3646.

Chen, H. & Zuo, J. M. (2007). *Structure and phase separation of Ag–Cu alloy thin films. Acta Mater.* **55**, 1617–1628.

Childs, P. A. & Misell, D. L. (1972). *Some aspects of elastic plural scattering of electrons by atoms. J. Phys. D Appl. Phys.* **5**, 2095.

Cockayne, D. J. H. (2007). *The study of nanovolumes of amorphous materials using electron scattering. Annu. Rev. Mater. Res.* **37**, 159–187.

Cockayne, D. J. H. & McKenzie, D. R. (1988). *Electron diffraction analysis of polycrystalline and amorphous thin films. Acta Cryst.* A**44**, 870–878.

Cowley, J. M. (1992). *Electron Diffraction Techniques*. International Union of Crystallography Monographs on Crystallography. Oxford: IUCr/Oxford University Press.

Cowley, J. M. (1995). *Diffraction Physics*. Amsterdam: Elsevier Science BV.

Cowley, J. M. (1999). *Electron nanodiffraction. Microsc. Res. Tech.* **46**, 75–97.

Cowley, J. M. & Hewat, A. W. (2004). *Powder and related techniques: electron and neutron techniques. International Tables for Crystallography* Vol. C, pp. 80–83. Dordrecht: Kluwer Academic Publishers.

Djerdj, I. & Tonejc, A. M. (2005). *Transmission electron microscopy studies of nanostructured TiO_2 films on various substrates. Vacuum*, **80**, 371–378.

Djerdj, I. & Tonejc, A. M. (2006). *Structural investigations of nanocrystalline TiO_2 samples. J. Alloys Compd.* **413**, 159–174.

Dollase, W. A. (1986). *Correction of intensities for preferred orientation in powder diffractometry: application of the March model. J. Appl. Cryst.* **19**, 267–272.

Egami, T. & Billinge, S. J. L. (2003). *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*. Oxford: Pergamon.

Egerton, R. F. (2011). *Electron Energy-Loss Spectroscopy in the Electron Microscope*. New York: Plenum Press.

Elsayedali, H. E. & Herman, J. W. (1990). *Ultrahigh vacuum picosecond laser-driven electron diffraction system. Rev. Sci. Instrum.* **61**, 1636–1647.

Faber, J. & Fawcett, T. (2002). *The Powder Diffraction File: present and future. Acta Cryst.* B**58**, 325–332.

Farrow, C. L. & Billinge, S. J. L. (2009). *Relationship between the atomic pair distribution function and small-angle scattering: implications for modeling of nanoparticles. Acta Cryst.* A**65**, 232–239.

Gammer, C. C., Mangler, C., Rentenberger, C. & Karnthaler, H. P. (2010). *Quantitative local profile analysis of nanomaterials by electron diffraction. Scr. Mater.* **63**, 312–315.

Gemmi, M. J., Fischer, J., Merlini, M., Poli, S., Fumagalli, P., Mugnaioli, E. & Kolb, U. (2011). *A new hydrous Al-bearing pyroxene as a water carrier in subduction zones. Earth Planet. Sci. Lett.* **310**, 422–428.

Gemmi, M., Voltolini, M., Ferretti, A. M. & Ponti, A. (2011). *Quantitative texture analysis from powder-like electron diffraction data. J. Appl. Cryst.* **44**, 454–461.

Gemmi, M., Zou, X. D., Hovmöller, S., Migliori, A., Vennström, M. & Andersson, Y. (2003). *Structure of Ti_2P solved by three-dimensional electron diffraction data collected with the precession technique and high-resolution electron microscopy. Acta Cryst.* A**59**, 117–126.

Gjonnes, K., Cheng, Y., Berg, B. S. & Hansen, V. (1998). *Corrections for multiple scattering in integrated electron diffraction intensities. Application to determination of structure factors in the [001] projection of Al_mFe. Acta Cryst.* A**54**, 102–119.

Gorelik, T., Matveeva, G., Kolb, U., Schleuss, T., Kilbinger, A. F. M., van de Streek, J., Bohled, A. & Brunklaus, G. (2010). *H-bonding schemes of di- and tri-p-benzamides assessed by a combination of electron diffraction, X-ray powder diffraction and solid-state NMR. CrystEngComm*, **12**, 1824–1832.

Gramm, F. C., Baerlocher, C., McCusker, L. B., Warrender, S. J., Wright, P. A., Han, B., Hong, S. B., Liu, Z., Ohsuna, T. & Terasaki, O. (2006). *Complex zeolite structure solved by combining powder diffraction and electron microscopy. Nature*, **444**, 79–81.

Haider, M. H., Rose, H., Uhlemann, S., Schwan, E., Kabius, B. & Urban, K. (1998). *A spherical-aberration-corrected 200 kV transmission electron microscope. Ultramicroscopy*, **75**, 53–60.

Henderson, R. (1995). *The potential and limitations of neutrons, electrons and X-rays for atomic resolution microscopy of unstained biological molecules. Q. Rev. Biophys.* **28**, 171–193.

Hill, R. J. & Howard, C. J. (1987). *Quantitative phase analysis from neutron powder diffraction data using the Rietveld method. J. Appl. Cryst.* **20**, 467–474.

Hirata, A., Hirotsu, Y., Ohkubo, T., Hanada, T. & Bengus, V. Z. (2006). *Compositional dependence of local atomic structures in amorphous $Fe_{100-x}B_x$ (x = 14, 17, 20) alloys studied by electron diffraction and high-resolution electron microscopy. Phys. Rev. B*, **74**, 214206.

Hirata, A. T., Morino, T., Hirotsu, Y., Itoh, K. & Fukunaga, T. (2007). *Local atomic structure analysis of Zr-Ni and Zr-Cu metallic glasses using electron diffraction. Mater. Trans.* **48**, 1299–1303.

references