2.8. Powder diffraction in external electric and magnetic fields

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2.8.1. Introduction

The functionality of materials depends strongly on the crystalline structure and structural changes during operation. The term 'structure' usually refers to the ideal structure, which specifies the positions of the atoms in a lattice, and thus the distances and angles between them. This idealized model is, however, far too simple to describe the full functionality of a material in a device. Many types of defects, such as point defects, dislocations or grain boundaries, are essential to the functionality and have to be taken into account. As the length scales of defects range from atomic bond lengths *via* nanometres to micrometres, different methods have to be used for comprehensive structural characterization. High-resolution transmission electron microscopy (HRTEM) is the ideal tool for studying a material at the atomic scale, as it gives direct evidence of the arrangement of atoms. In addition, information on the chemical composition can be provided through X-ray or electron spectroscopies. However, in many cases electron microscopy requires a tremendous effort in sample preparation. Furthermore, the application of electric fields in a TEM column is a serious challenge with significant limitations. While electron microscopy will provide information on small sample volumes, diffraction methods probe larger quantities of samples, but give average information. In general, diffraction methods are based on electromagnetic or particle waves. X-ray photons with energies in the keV range have wavelengths similar to interatomic distances and, therefore, X-rays from laboratory sources or synchrotrons are the most widely used. Thermal neutrons with meV energies have complementary properties suited for other applications. While electrons are usually used for microscopy techniques, the field of electron crystallography has developed in recent years. However, given the very small size of an electron beam, its short wavelength (*circa* 0.03 Å) and high absorption, most particles studied by electron crystallography can be considered as single crystals. The combination of electron crystallography and powder diffraction is a powerful tool for tiny crystalline samples, especially inclusions (Weirich *et al.*, 2006).

In the field of *in situ* materials research, multiparametric measurements as functions of three or more external parameters, *e.g.* temperature–magnetic field–pressure or temperature–magnetic field–electric field, have been reported. However, the majority of so-called *in situ* studies are carried out as a function of temperature and sometimes of external pressure. Studies of structural changes under electric fields are relatively rare. Studies of changes due to magnetic fields almost entirely lie in the domain of neutron scattering, where single-crystal experiments usually give more details on the evolution of the magnetic structure. The challenges, necessary instrumentation and some examples of *in situ* diffraction measurements are described in Chapter 16 of the book *Modern Diffraction Methods* (Mittemeijer & Welzel, 2012).

2.8.2. Experimental conditions

Several challenges have to be overcome for experiments under external fields, so the exerimental conditions have to be adapted accordingly. As all these experiments are based on time-dependent conditions, the first requirement is a detecting system that allows fast data acquisition. Considerable progress in recent years has made time resolution of the order of nanoseconds possible (Schmitt *et al.*, 2007), thus enabling stroboscopic diffraction experiments. Higher time resolutions are possible with careful synchronization of the experiment with the time structure of a synchrotron X-ray beam. The electron bunches in a synchrotron are usually separated by several tens to hundreds of nanoseconds and have a width in the range of picoseconds. Once the gating window of an experiment is smaller than the time between successive bunches, the time resolution immediately reaches the width of a bunch. Structural responses to external stimuli are related to displacements of atoms and changes in unit-cell distortion (*i.e.* lattice parameters). The displacements are fairly small and thus very high sensitivity is a prerequisite. In order to study small unit-cell distortions, very good angular resolution is mandatory. The potential angular resolution that is possible in synchrotron experiments is very often not reached for powder samples, as the half-widths of the reflections are mainly determined by the microstructure.

In monochromatic neutron diffraction, the greater divergence of a neutron beam compared to a synchrotron beam and its spectral width ($\Delta\lambda/\lambda$) usually only allow a resolution in the range $\Delta d/d \simeq 10^{-2}$ to be achieved with medium-resolution (high-intensity) diffractometers; this can be tuned down to $\Delta d/d \simeq 10^{-3}$ by tightening the beam collimation at high-resolution monochromatic instruments. Significantly better resolution of $\Delta d/d \simeq 4 \times 10^{-4}$ can be achieved by combining the neutron time-of-flight technique with long neutron flight paths (*circa* 100 m) in back-scattering geometry. Even higher $\Delta d/d$ values (potentially down to 10^{-6}) can be obtained using the spin-echo-based neutron-scattering technique called Larmor diffraction (Repper *et al.*, 2009). The advantages of neutrons over X-rays are that they penetrate more deeply through materials, their scattering form factors are nearly independent of momentum transfer, and they are sensitive to the isotopic composition of a material, enabling accurate location of light elements in the presence of heavy ones, as well as the ability to distinguish between neighbouring elements in the periodic table. Whereas both synchrotron radiation and neutron scattering may be used to elucidate crystal structures under an electric field, neutrons can also be used to study magnetic order and its modification under a magnetic field. Therefore, the examples listed here for studies under electric fields use both kinds of radiation, whereas the examples of studies involving magnetic fields mainly use neutron scattering.

The properties of the materials discussed in this chapter are intimately related to their crystal structures; hence, any change in crystal structure is immediately reflected in the properties. The examples we have chosen are dominated by ferroelectric ceramics and lithium-ion battery materials on the one hand and multiferroic materials on the other.

Most reports in the literature on *in situ* or *in operando* studies deal either with the kinetics of chemical reactions (intercalation, crystallization, catalysis) or structural changes of materials under varying external conditions (temperature, pressure *etc.*). This

references