

## 3.3. POWDER DIFFRACTION PEAK PROFILES

$$\Delta 2\theta = 360s \cos \theta / \pi R, \quad (3.3.13)$$

where  $R$  is the goniometer radius. This is the major peak-displacement effect and can be detected for sample displacements as small as  $10 \mu\text{m}$ .

A similar effect can be observed for Debye–Scherrer instrumentation when the goniometer axis is not coincident with the sample axis; this is a more common problem for neutron powder diffraction instruments where accurate placement of very massive goniometers can be difficult. In this case the peak displacement is

$$\Delta 2\theta = \frac{180}{\pi R} (s_x \cos 2\theta + s_y \sin 2\theta), \quad (3.3.14)$$

where  $s_x$  and  $s_y$  are displacements perpendicular and parallel to the incident beam, respectively, all in the diffraction plane.

In high-resolution instrumentation (even at a synchrotron) goniometer axis displacements less than  $10 \mu\text{m}$  can be detected.

Specimen transparency in Bragg–Brentano diffraction can also cause peak displacements arising from the shift in effective sample position to below the surface at high scattering angles. This shift for a thick specimen is

$$\Delta 2\theta = 90 \sin 2\theta / \mu_{\text{eff}} \pi R, \quad (3.3.15)$$

where  $\mu_{\text{eff}}$  is the effective sample absorption coefficient taking into account the packing density.

## 3.3.2.4. Fundamental parameters profile modelling

An alternative method for describing the source and instrumental part of the powder peak profile is to develop a set of individual functions that form the part of the profile arising from each of the instrumental components that shape the beam profile (Cheary & Coelho, 1992, 1998*a,b*). Ideally, each function is parameterized in terms of the physical parameters of the corresponding instrument component (*e.g.* slit width and height, sample dimensions and absorption, source size and emission characteristics, *etc.*), which are known from direct measurement. The set of functions are then convoluted *via* fast mathematical procedures to produce a line profile that matches the observed one. Any remaining profile-broadening parameters (*e.g.* for sample crystallite size and microstrain, see Section 3.3.5 for details) are then allowed to adjust during a Rietveld refinement. By employing this fundamental parameters (FP) approach, these parameters are unaffected by any instrumental parameterization.

The FP method offers two clear advantages over the more empirical approach outlined in Sections 3.3.2.1–3.3.2.3 above: (i) it can more closely describe the actual instrumental effects that contribute to the profile shape, thus improving the precision of the fit to the observed data and (ii) it can be used to describe a source characteristic or an instrumental arrangement that is outside the normally used configuration, yielding a result that would be difficult to obtain otherwise (Cheary *et al.*, 2004).

## 3.3.3. Peak profiles for neutron time-of-flight experiments

## 3.3.3.1. The experiment

The neutron source in a time-of-flight (TOF) powder diffraction experiment produces pulses of polychromatic neutrons; these travel over the distance from the source to the sample and then to the detectors which are placed at fixed scattering angles about the sample position; the travel times are of the order of 1–100 ms. This has been briefly described in Volume C of *Inter-*

*national Tables for Crystallography* (Jorgensen *et al.*, 1992). Because neutrons of differing velocities ( $v$ ) have differing wavelengths ( $\lambda$ ) according to the de Broglie relationship ( $\lambda = h/mv$ ) given Planck's constant ( $h$ ) and the neutron mass ( $m$ ), they will sort themselves out in their time of arrival at the detector. The powder pattern appears as a function of TOF *via* Bragg's law ( $\lambda = 2d \sin \theta$ ) in which the wavelength is varied and  $\theta$  is fixed. The approximate relationship between TOF, wavelength and  $d$ -spacing observed in a particular detector can be derived from the de Broglie relationship and Bragg's law to give

$$\text{TOF} = 252.7784L\lambda = 505.5568Ld \sin \theta. \quad (3.3.16)$$

The constants are such that given  $\lambda$  in ångströms and the total neutron flight path length  $L$  in metres, then the TOF will be in  $\mu\text{s}$ . An analysis of the possible variances in these components then gives an estimate of the powder diffraction peak widths:

$$\Delta d/d = [(\Delta t/t)^2 + (\Delta \theta \cot \theta)^2 + (\Delta L/L)^2]^{1/2}, \quad (3.3.17)$$

where  $\Delta d$ ,  $\Delta t$ ,  $\Delta \theta$  and  $\Delta L$  are, respectively, the uncertainties in  $d$ -spacing, TOF, scattering angle  $\theta$  and total flight path  $L$  (Jorgensen & Rotella, 1982). Consequently, these three terms also determine the instrumental contribution to the neutron TOF powder peak profile.

## 3.3.3.2. The neutron pulse shape

The neutron pulse shape depends on the mode of production. Early studies (Buras & Holas, 1968; Turberfield, 1970) used one or more choppers to define a polychromatic pulse from a reactor source, resulting in essentially Gaussian powder peak profiles whose FWHM ( $\Gamma_G$ ) is nearly constant ( $B \simeq 0$ ):

$$\Gamma_G^2 = A + Bd^2, \quad (3.3.18)$$

so that the Rietveld technique can easily be used (*e.g.* Worlton *et al.*, 1976). Unfortunately, this approach gave very low intensities and relatively low resolution powder patterns.

A more useful approach uses a spallation source to produce the pulsed neutron beam. Neutrons are produced when a high-energy proton beam ( $>500 \text{ MeV}$ ) strikes a heavy metal target (usually W, U or liquid Hg) *via* a spallation process (Carpenter *et al.*, 1984). These very high energy neutrons strike small containers of moderating material (usually  $\text{H}_2\text{O}$ , liquid  $\text{CH}_4$  or liquid  $\text{H}_2$ ) which then comprise the neutron source seen by the powder diffraction instrument. The entire target/moderator system is encased in a neutron-reflective material (usually Be) to enhance the neutron flux and then further encased in a biological shield. Each moderator may be encased on the sides away from the instrument (*e.g.* powder diffractometer) in a thin neutron absorber (*e.g.* Cd or Gd) and may also contain an inner absorber layer ('poison') to sharpen the resulting pulse of thermal neutrons. These sources produce a polychromatic neutron beam that is rich in both thermal ( $<300 \text{ meV}$ ) and epithermal ( $>300 \text{ meV}$ ) neutrons. The proton pulses can have a very short duration ( $\sim 200 \text{ ns}$ ) (from a 'short-pulse' source, *e.g.* ISIS, Rutherford Laboratory, UK or LANSCE, Los Alamos National Laboratory, USA) or a much longer duration ( $>500 \text{ ns}$ ) (a 'long-pulse' source, *e.g.* SNS, Oak Ridge National Laboratory, USA or ESS, European Spallation Source, Sweden); the pulse repetition rate at these sources is 10–60 Hz. These characteristics are largely dictated by the proton accelerator and neutron source design. The resulting neutron pulse results from complex down-scattering and thermalization processes in the whole target/moderator assembly; it may be further shaped by choppers,