3.3. Powder diffraction peak profiles

R. B. Von Dreele

3.3.1. Introduction

The analysis of a powder diffraction pattern usually involves the fitting of a model to the set of peaks that are found in that pattern. The desired result may be accurate peak positions to be used as input for an indexing procedure, or extraction of the suite of reflection intensities for crystal structure determination or a Rietveld refinement. In any case, a good description of the shape of the powder peak profile and how it varies across the entire pattern is of paramount importance for obtaining the highest-quality results, and this topic was briefly reviewed in Volume C of *International Tables for Crystallography* (Parrish, 1992).

The fitting is a least-squares procedure in which the model used to calculate the intensity of the profile is

$$Y(x) = \sum_j I_j P_j(\Delta) + B(x), \qquad (3.3.1)$$

where I_j is the integrated intensity of the jth peak and P is the shape function for that peak, which depends on the offset ($\Delta = x - T_j$) of its position T_j from the observation point x. The sum is over all reflections that could contribute to the profile and $B(x)$ is a background intensity function. The observed shape of the peaks arises from a convolution of the intrinsic source profile (G_λ), the various instrumental profile contributions (G_I) (*e.g.* from slits and monochromators, discussed in Chapter 3.1) and the characteristics of the sample (G_S) that broaden the idealized reciprocal-space points (see Chapter 3.6):

$$P(\Delta) = G_\lambda * G_I * G_S. \qquad (3.3.2)$$

In practice, the peak profile function is usually developed by either selecting a peak-shape function that has the required shape characteristics to fit the experimental peak profiles (the semi-empirical function approach, or SFA) or by selecting a number of contributing functions and doing the requisite convolutions (the fundamental parameters approach, or FPA) (Cheary & Coelho, 1998*b*).

Both approaches have been used for the analysis of constant-wavelength neutron and X-ray powder diffraction data and for neutron time-of-flight (energy-dispersive) powder data. In addition, the peaks can be seen to be displaced from their expected positions given by Bragg's law. As we will see, this displacement is partially a consequence of some geometric features of the experiment but is also dependent upon the particular description of the peak profile.

3.3.2. Peak profiles for constant-wavelength radiation (X-rays and neutrons)

3.3.2.1. *Introduction – symmetric peak profiles*

The realization that the neutron powder diffractometer at the Reactor Centrum Nederland, Petten, produced powder peak profiles that were Gaussian in shape led Rietveld (1967) to develop a full-pattern method for crystal structure refinement (Rietveld, 1967, 1969), now known as the Rietveld refinement method. The Gaussian is formulated as

$$
\begin{aligned}
P_G(\Delta, \Gamma_G \text{ or } \sigma^2) &= \frac{(8\ln 2)^{1/2}}{\Gamma_G(2\pi)^{1/2}} \exp\left(\frac{-4\ln 2\Delta^2}{\Gamma_G^2}\right) \\
&= \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(\frac{-\Delta^2}{2\sigma^2}\right),
\end{aligned}
\qquad (3.3.3)
$$

where the width of the peak is expressed as either the full width at half-maximum (FWHM = Γ_G) or as the variance (σ^2). Rietveld also recognized the earlier analysis of the resolution of a neutron powder diffractometer by Caglioti *et al.* (1958), who showed that the contributions from the source size, collimators and monochromator crystal mosaic spread and scattering angle could be combined analytically to give

$$\Gamma_G^2 = U \tan^2\theta + V \tan\theta + W \qquad (3.3.4)$$

with U, V and W adjustable during the Rietveld refinement. A modified form of this may have more stability in refinement (attributed to E. Prince by Young & Wiles, 1982):

$$\Gamma_G^2 = U'(\tan\theta - K_0)^2 + V'(\tan\theta - K_0) + W', \qquad (3.3.5)$$

where K_0 is arbitrarily chosen as 0.6.

Improvements in the resolution of neutron powder diffractometers and (more importantly) attempts to apply the Rietveld method to X-ray powder diffraction data required the development of new powder profile functions (Malmros & Thomas, 1977; Young *et al.*, 1977; Young & Wiles, 1982); this is because the Gaussian function [equation (3.3.3)] gave poor fits to observed peak profiles, partially because of the Lorentzian emission line profile (G_λ) from laboratory X-ray tubes. Many functions were considered, including Lorentzian ('Cauchy'), various modified Lorentzians, Pearson VII and pseudo-Voigt. Of these the last two performed (on individual peak fits) about equally well; functional forms are:

Lorentzian 'Cauchy' function

$$P_L(\Delta, \Gamma_L) = \left(\frac{\Gamma_L}{2\pi}\right)\left\{\frac{4}{\left[\Gamma_L^2 + (2\Delta)^2\right]}\right\}, \qquad (3.3.6)$$

Pearson VII function

$$P_{\text{P7}}(\Delta, \xi, \mu) = \frac{\Gamma(\mu)}{\xi\Gamma\left(\mu - \frac{1}{2}\right)(\mu\pi)^{1/2}} \bigg/ \left(1 + \frac{\Delta^2}{\mu\xi^2}\right)^\mu, \qquad (3.3.7)$$

pseudo-Voigt function

$$P_{\text{PV}}(\Delta, \Gamma, \eta) = \eta P_L(\Delta, \Gamma) + (1 - \eta)P_G(\Delta, \Gamma), \qquad (3.3.8)$$

where Γ_L is the FWHM of the Lorentzian peak and $\Gamma(\mu)$ in the Pearson VII function is the Gamma function; μ may vary between 0 and ∞, and μ is the half width at $(1 + 1/\mu)^{-\mu}$ of the peak height (David, 1986); $P_{\text{P7}}(\Delta, \Gamma, 1) \simeq P_L(\Delta, \Gamma)$ and $P_{\text{P7}}(\Delta, \Gamma, \infty) \simeq P_G(\Delta, \Gamma)$. Although the Pearson VII function performs well in individual peak fits, it is of little use for Rietveld refinements because of the difficulty in relating its coefficients to physically meaningful characteristics of the sample and will not be considered further in this discussion.