8.6. THE RIETVELD METHOD

Profile R factor:

$$R_P = \frac{\sum_i |y_i(\text{obs.}) - y_i(\text{calc.})|}{\sum_i y_i(\text{obs.})}.$$

Weighted profile R factor:

$$R_{wP} = \left[\frac{\sum_i w_i |y_i(\text{obs.}) - y_i(\text{calc.})|^2}{\sum_i w_i y_i^2(\text{obs.})} \right]^{1/2}.$$

Bragg R factor:

$$R_I = \frac{\sum_k |I_k(\text{obs.}) - I_k(\text{calc.})|}{\sum_k I_k(\text{obs.})}.$$

Expected R factor:

$$R_E = \left[\frac{\mathcal{N} - P}{\sum_i w_i y_i^2(\text{obs.})} \right]^{1/2}.$$

I_k is the integrated intensity of the kth reflection, $\mathcal{N}$ is the number of independent observations, and P is the number of refined parameters. The most important indicators are R_{wP} and R_E. The ratio R_{wP}/R_E is the so-called 'goodness-of-fit', χ^2: in a successful refinement χ^2 should approach unity. The Bragg R factor is useful, since it depends on the fit of the structural parameters and not on the profile parameters.

8.6.2. Problems with the Rietveld method

One should be aware of certain problems that may give rise to failure in a Rietveld refinement.

8.6.2.1. *Indexing*

The first step in refinement is the indexing of the pattern. As the Rietveld method is often applied to the refinement of data for which the unit-cell parameters and space group are already known, there is then little difficulty in indexing the pattern, provided that there are a few well resolved lines. Without this knowledge, the indexing requires, as a starting point, the measurement of the d values of low-angle diffraction lines to high accuracy. According to Shirley (1980): 'Powder indexing works beautifully on good data, but with poor data it usually will not work at all'. The indexing of powder patterns and associated problems are discussed by Shirley (1980), Pawley (1981), Cheetham (1993) and Werner (2002).

8.6.2.2. *Peak-shape function (PSF)*

The appropriate function to use varies with the nature of the experimental technique. In addition to the Gaussian PSF in (8.6.1.3), functions commonly used for angle-dispersive data are (Young & Wiles, 1982):

$$G_{ik} = \frac{2}{\pi H_k} \left[1 + 4\left(\frac{\Delta 2\theta_{ik}}{H_k}\right)^2 \right]^{-1} \qquad \text{(Lorentzian)}$$

$$G_{ik} = \frac{2\eta}{\pi H_k} \left[1 + 4\left(\frac{\Delta 2\theta_{ik}}{H_k}\right)^2 \right]^{-1}$$
$$+ (1 - \eta) \frac{2\sqrt{\ln 2}}{\sqrt{\pi} H_k} \exp\left[-4\ln 2 \left(\frac{\Delta 2\theta_{ik}}{H_k}\right)^2 \right] \qquad \text{(pseudo-Voigt)}$$

$$G_{ik} = \frac{2\Gamma(n)(2^{1/n} - 1)}{\pi H_k \Gamma(n - \frac{1}{2})} \left[1 + 4(2^{1/n} - 1)\left(\frac{\Delta 2\theta_{ik}}{H_k}\right)^2 \right]^{-n}$$
$$\text{(Pearson VII)}$$

where $\Delta 2\theta_{ik} = 2\theta_i - 2\theta_k$. η is a parameter that defines the fraction of Lorentzian character in the pseudo-Voigt profile. $\Gamma(n)$ is the gamma function: when $n = 1$, Pearson VII becomes a Lorentzian, and when $n = \infty$, it becomes a Gaussian.

The tails of a Gaussian distribution fall off too rapidly to account for particle size broadening. The peak shape is then better described by a convolution of Gaussian and Lorentzian functions [*i.e.* Voigt function: see Ahtee, Nurmela & Suortti (1984) and David & Matthewman (1985)]. A pulsed neutron source gives an asymmetrical line shape arising from the fast rise and slow decay of the neutron pulse: this shape can be approximated by a pair of exponential functions convoluted with a Gaussian (Albinati & Willis, 1982; Von Dreele, Jorgensen & Windsor, 1982).

The pattern from an X-ray powder diffractometer gives peak shapes that cannot be fitted by a simple analytical function. Will, Parrish & Huang (1983) use the sum of several Lorentzians to express the shape of each diffraction peak, while Hepp & Baerlocher (1988) describe a numerical method of determining the PSF. Pearson VII functions have also been successfully used for X-ray data (Immirzi, 1980). A modified Lorentzian function has been employed for interpreting data from a Guinier focusing camera (Malmros & Thomas, 1977). PSFs for instruments employing X-ray synchrotron radiation can be represented by a Gaussian (Parrish & Huang, 1980) or a pseudo-Voigt function (Hastings, Thomlinson & Cox, 1984).

8.6.2.3. *Background*

The background may be determined by measuring regions of the pattern that are free from Bragg peaks. This procedure assumes that the background varies smoothly with $\sin\theta/\lambda$, whereas this is not the case in the presence of disorder or thermal diffuse scattering (TDS), which rises to a maximum at the Bragg positions. An alternative approach is to include a background function in the refinement model (Richardson, 1993). If the background is not accounted for satisfactorily, the temperature factors may be incorrect or even negative. The various procedures for estimating the background for X-ray, synchrotron, constant-wavelength and TOF neutron powder patterns are reviewed by McCusker *et al.* (1999).

In neutron diffraction, the main contribution to the background from hydrogen-containing samples is due to incoherent scattering. Deuterating the sample is essential in order to substantially reduce this background.