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8.6. The Rietveld method

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In the Rietveld method of analysing powder diffraction data, the crystal structure is refined by fitting the entire profile of the diffraction pattern to a calculated profile. There is no intermediate step of extracting structure factors, and so patterns containing many overlapping Bragg peaks can be analysed. The method was applied originally by Rietveld (1967, 1969) to the refinement of neutron intensities recorded at a fixed wavelength. Subsequently, it has been used successfully for analysing powder data from all four categories of experimental technique, with neutrons or X-rays as the primary radiation and with scattered intensities measured at a fixed wavelength (and variable scattering angle) or at a fixed scattering angle (and variable wavelength).

Powder refinements are usually less satisfactory than those on single-crystal data, as the three-dimensional information of the reciprocal lattice is compressed into one dimension in the powder pattern. Nevertheless, a large number of successful refinements by the Rietveld method has been reported; reviews have been given by Taylor (1985), Hewat (1986), Cheetham & Wilkinson (1992), Young (1993), Harris & Tremayne (1996), Masciocchi & Sironi (1997), Harris *et al.* (2001) and David *et al.* (2002). Here we shall discuss only the basic principles of the refinement procedure.

8.6.1. Basic theory

The model of the structure is refined by least-squares minimization of the residual

$$M = \sum_{i=1}^{N} w_i \left[y_i(\text{obs.}) - y_i(\text{calc.}) \right]^2. \qquad (8.6.1.1)$$

y_i(obs.) is the intensity measured at a point i in the diffraction pattern corrected for the background intensity b_i, w_i is its weight, and y_i(calc.) is the calculated intensity. If the background at each point is assumed to be zero, and if the only source of error in measuring the intensities is that from counting statistics, the weight is given by

$$w_i = \left[y_i(\text{obs.}) \right]^{-1}.$$

The summation in (8.6.1.1) runs over all N data points. The number of data points can be arbitrarily increased by reducing the interval between adjacent steps. However, this does not necessarily imply an improvement in the standard uncertainties (s.u.'s; see Section 8.1.2) of the structural parameters (see Subsection 8.6.2.5), which are dependent on the number of linearly independent columns in the design matrix [equation (8.1.2.3)]. The number of independent observations in a powder pattern is determined by the extent of overlapping of adjacent reflections. An intuitive argument for estimating this number has been proposed by Altomare *et al.* (1995) and a more rigorous statistical estimate has been described by Sivia (2000). The strategy for choosing the number of steps and apportioning the available counting time has been discussed by McCusker *et al.* (1999) and references therein. The relation between counting statistics and the s.u.'s has been discussed by Baharie & Pawley (1983) and by Scott (1983).

The calculated intensity is evaluated using the equation

$$y_i(\text{calc.}) = s \sum_{k=k_1}^{k_2} m_k L_k \left| F_k \right|^2 G_{ik}, \qquad (8.6.1.2)$$

where s is a scale factor, m_k is the multiplicity factor for the kth reflection, L_k is the Lorentz–polarization factor, F_k is the structure factor and G_{ik} is the 'peak-shape function' (PSF). The summation in (8.6.1.2) is over all nearby reflections, k_1 to k_2, contributing to a given data point i.

A fundamental problem of the Rietveld method is the formulation of a suitable peak-shape function. For X-rays, a mixture of Gaussian and Lorentzian components is sometimes used (see Subsection 8.6.2.2). For neutrons, it is easier to find a suitable analytical function, and this is, perhaps, the main reason for the initial success of neutron Rietveld analysis. For a neutron diffractometer operating at a fixed wavelength and moderate resolution, the PSF is approximately a Gaussian of the form

$$G_{ik} = \frac{2}{H_k} \sqrt{\frac{\ln 2}{\pi}} \exp\left[-\frac{4 \ln 2 \, (2\theta_i - 2\theta_k)^2}{H_k^2} \right], \qquad (8.6.1.3)$$

where H_k is the full width at half-maximum (FWHM) of the peak, $2\theta_i$ is the scattering angle at the ith point, and θ_k is the Bragg angle for reflection k.

The angular dependence of the FWHM for a Gaussian peak-shape function can be written in the form

$$H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W,$$

where U, V and W are half-width parameters independent of θ_k (Caglioti, Paoletti & Ricci, 1958). To allow for intrinsic sample broadening and instrumental resolution, U, V and W are treated as adjustable variables in the least-squares refinement. The tails of a Gaussian peak decrease rapidly with distance from the maximum, and the intensity at one-and-a-half times the FWHM from the peak is only about 0.2% of the intensity at the peak. Thus, no large error is introduced by assuming that the peak extends over a range of approximately $\pm 1.5 H_k$ and is cut off outside this range. The FWHM for the Lorentzian (see Subsection 8.6.2.2) can be modelled by the relation

$$H_k = X \tan \theta_k + Y / \cos \theta_k.$$

The Lorentzian function extends over a much wider range than the Gaussian. A more flexible approach to this line-broadening problem is described by McCusker *et al.* (1999).

The least-squares parameters are of two types. The first contains the usual structural parameters: for example, fractional coordinates of each atom in the asymmetric unit and the corresponding isotropic or anisotropic displacement parameters. The second type represents 'profile parameters' which are not encountered in a least-squares refinement of single-crystal data. These include the half-width parameters and the dimensions of the unit cell. Further parameters may be added to both groups allowing for the modelling of the background and for the asymmetry of the reflections. The maximum number of parameters that can be safely included in a Rietveld refinement is largely determined by the quality of the diffraction pattern, but intrinsic line broadening will set an upper limit to this number (Hewat, 1986).

The following indicators are used to estimate the agreement with the model during the course of the refinement.

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Profile R factor:

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

Weighted profile R factor:

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

Bragg R factor:

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

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):

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

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

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

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.

references