

## Accurate Structure Factor Measurements by Powder Methods\*

*T. M. Sabine*

University of Technology, Sydney, P.O. Box 123,  
Broadway, N.S.W. 2007, Australia.

### *Abstract*

Powder diffraction data are normally analysed by Rietveld refinement. In this technique the observed diffraction pattern is fitted to a calculated pattern by least-squares methods. The accuracy with which structure factors can be determined is dependent on the parameters in the model being an accurate representation of the physical situation. The Rietveld model is derived in the kinematic approximation. Deviations from kinematic behaviour because of extinction, absorption, thermal diffuse scattering, and multiple scattering are then included in the model. As a test of the method the Debye-Waller factor (which is the only unknown component of the structure factor) is determined for magnesium oxide from time-of-flight neutron data on four specimens of very different grain size.

### 1. Introduction

The Rietveld (1969) method has become widely used as a procedure for extracting crystallographic information from powder data. In this method the quantity

$$M = \sum_i w_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2 \quad (1)$$

is minimised, where  $y_i^{\text{obs}}$  is the number of neutrons scattered into the  $i$ th time or angle channel and  $y_i^{\text{calc}}$  is the number that would have been scattered into that channel if the model of the sample and the instrument were correct. The weight  $w_i$  of the  $i$ th observation is taken as the reciprocal of the variance of  $y_i^{\text{obs}}$ . The assumption that the minimisation of (1) leads to the best least-squares estimate of the parameters of the model is critically dependent on the physical reality of the model from which  $y_i^{\text{calc}}$  is obtained.

In this paper  $y_i^{\text{calc}}$  is formulated for data obtained by neutron time-of-flight methods from a randomly oriented powder specimen. It is assumed that the material is non-magnetic and defect free. The statistical basis of the Rietveld method is discussed and an analysis is made of time-of-flight data from magnesium oxide.

### 2. Kinematic Approximation

In this approximation the intensity of radiation scattered by a crystal is proportional to the intensity scattered by one unit cell multiplied by the number of unit cells in the

\* Paper presented at the International Symposium on Accuracy in Structure Factor Measurement, held at Warburton, Australia, 23-26 August 1987.

crystal. The diffraction pattern which would be observed is calculated in this section. It is assumed that each lattice site is occupied by an atom, and also that the detection system records all scattered neutrons without regard to an energy change produced by the interaction. This is the frozen crystal case in which dynamic fluctuations, such as thermal vibrations, appear as static displacements (Gurevich and Tarasov 1968).

The starting point is the differential cross section for coherent elastic scattering into a single Bragg reflection. Neglecting the effect of finite crystal size, we have

$$\frac{d\sigma}{d\Omega} = N_c^2 V F^2 \delta(k - k_B), \quad (2)$$

where  $N_c$  is the number of unit cells per unit volume,  $V$  is the volume of the crystal, and  $F$  is the structure factor magnitude per unit cell and is assumed to include the Debye-Waller factor. The incident beam has the wave vector  $k_i$  and the scattered neutron  $k_f$ . The magnitude of both these vectors is  $\lambda^{-1}$  where  $\lambda$  is the neutron wavelength. The scattering vector is given by  $k = k_f - k_i$ , and has the magnitude  $2 \sin \theta / \lambda$  where  $2\theta$  is the scattering angle. The value of the scattering vector at the exact Bragg position is  $k_B$ , which has a magnitude  $d^{-1}$  where  $d$  is the interplanar spacing.

To determine the total cross section per unit volume  $\sigma$  for Bragg scattering into a single reflection, as required in Section 3, we must carry out an integration of  $\delta(k - k_B)$  over  $d\Omega$ , which is an elementary area at the tip of  $k_f$ . The result is

$$\sigma = N_c^2 F^2 \lambda^2 \delta(k - k_B) / \sin \theta. \quad (3)$$

Integration over the remaining delta function leads, in a straightforward way, to the usual expressions for the integrated intensity from single crystals.

When the specimen is a randomly oriented powder  $k_B$  can take up all orientations relative to  $k$  with equal probability. Then, after averaging, we get

$$\begin{aligned} \langle \delta(k - k_B) \rangle &= \frac{1}{4\pi k_B^2} \delta(k - k_B), \\ \frac{d\sigma}{d\Omega} &= \frac{N_c^2 V F^2}{4\pi k_B^2} \delta(k - k_B). \end{aligned} \quad (4)$$

The total cross section for scattering into a Debye-Scherrer ring, required in Section 3, is given by the integration of (4) over  $d\Omega$ :

$$\sigma_{\text{tot}} = N_c^2 V F^2 \lambda^2 / 2 k_B. \quad (5)$$

### 3. Deviations from the Kinematic Approximation

The kinematic approximation assumes that the intensity of the diffracted beam increases linearly with the volume of the crystal. This would require that each unit cell is exposed to the full intensity of the incident beam, and that the diffracted beam is not attenuated by scattering in its passage through the crystal. Neither of these assumptions is realistic. The interplay between the diffracted and incident beam is

expressed by the Darwin (1922) intensity equations

$$\frac{\partial I_i}{\partial t_i} = -\sigma I_i + \sigma I_f, \quad \frac{\partial I_f}{\partial t_f} = -\sigma I_f + \sigma I_i, \quad (6, 7)$$

where  $I_i$  is the intensity in the incident beam along  $t_i$ , while  $I_f$  is the intensity in the diffracted beam along  $t_f$ . The quantity  $\sigma$  is the interaction cross section per unit volume. The total scattered intensity is  $I_f$  integrated over the exit surface of the crystal. These equations have exact solutions only in the Laue ( $2\theta = 0^\circ$ ) case and the Bragg ( $2\theta = 180^\circ$ ) case (Zachariasen 1945; Hamilton 1957). The use of these limiting solutions will be indicated by the subscripts L and B respectively.

(a) *Extinction*

The solution of (6) and (7) as given above is appropriate to the phenomenon of extinction. Extinction is customarily classified as primary or secondary. Primary extinction is the reduction of intensity of the Bragg reflected beam by re-scattering into the direction of the incident beam as it passes through successive planes in a perfect crystal. Secondary extinction results from the presence in the crystal of mosaic blocks of identical orientation. The Bragg reflected beam from one mosaic block will be depleted by scattering into the primary beam direction by a block of the same orientation.

Primary extinction is proportional to the size of the perfect crystal block, while secondary extinction is proportional to the closeness in orientation of successive blocks. In random powders the only extinction mechanism is primary extinction within individual grains.

When extinction is present, the intensity of the diffracted beam is less than that calculated from the kinematic approximation. This intensity loss is balanced by the increase in the intensity of the transmitted beam. There is no additional diffuse scattering.

The extinction coefficient is defined by

$$I^{\text{obs}} = EI^{\text{kin}}, \quad (8)$$

where  $I^{\text{obs}}$  is the observed intensity while  $I^{\text{kin}}$  is the intensity in the kinematic approximation. Using equation (3) and the solutions of (6) and (7) as a starting point, Sabine (1988) has given formulae for  $E$ :

$$E = E_L \cos^2 \theta + E_B \sin^2 \theta; \quad (9)$$

$$E_L = 1 - \frac{x}{2} + \frac{x^2}{4} - \frac{5x^3}{48} + \frac{7x^4}{192}, \quad x < 1$$

$$= \left( \frac{2}{\pi x} \right)^{\frac{1}{2}} \left( 1 - \frac{1}{8x} - \frac{3}{128x^2} - \frac{3}{1024x^3} \right), \quad x > 1,$$

$$E_B = 1/(1+x)^{\frac{1}{2}}.$$

In these expressions  $x = (KN_c \lambda F D)^2$ , and  $D$  is the refinable parameter, of the order of the average mosaic block size in the specimen. The structure factor  $F$  includes the

Sabine and Clarke (1977) and Sabine (1980) have generalised the incoherent component to include all sources of diffuse scattering. In the present case of a defect free non-magnetic crystal the components are thermal diffuse scattering, incoherent scattering and multiple scattering. These sum to give, using the incoherent approximation of Marshall and Stuart (1959),

$$y^D = \frac{N_c V I(\lambda) \text{wh} d\lambda}{4\pi R^2} \left( \sum_{\text{incoh}} + \sum_{\text{coh}} (1-M) e^{-2W(\lambda)} + \sum_{\text{coh}} (1-e^{-2W(\lambda)}) \right). \quad (16)$$

The Debye-Waller factor is  $e^{-2W(\lambda)}$ .

Use of the incoherent approximation for thermal diffuse scattering over the complete range of time-of-flight data is the least satisfactory aspect of equation (16). At long times, corresponding to large  $d$  spacings, one-phonon scattering which peaks at the Bragg positions will predominate. At short times, the major part of the inelastic scattering will result from multi-phonon processes. Multi-phonon scattering is spread approximately uniformly in the pattern.

### (c) Total Ordinate

The value of the total calculated ordinate for the scattering angle  $2\theta$  is given by

$$y_i^{\text{calc}} = S I(\lambda) A(\lambda) d\lambda \times \left( \sum_k p_k N_c \lambda^4 E_k(\lambda) M_k(\lambda) G_{ik}(\Delta\lambda) L_k F_k^2 + b(\lambda) \right). \quad (17)$$

The index  $k$  runs over all overlapping reflections. In equation (17)  $S = N_c V \text{wh}/4\pi R^2$  is a scale factor,  $L_k = 1/8 \sin^3 \theta$  is the Lorentz factor,  $A(\lambda)$  is the absorption factor from (11),  $E(\lambda)$  is the extinction factor from (9),  $M(\lambda)$  is the multiple scattering factor from (13),  $p_k$  is the multiplicity of the  $k$ th reflection of the structure factor  $F_k$  (the Debye-Waller factor is included in  $F_k$ ),  $G_{ik}(\Delta\lambda)$  is the profile function for the  $k$ th reflection evaluated at the  $i$ th ordinate in the diffraction pattern and, finally,  $b(\lambda)$  is the quantity enclosed by the large parentheses in equation (16). The instrumental background has been ignored.

### (d) An Absolute Scale

An absolute scale can be found by evaluating  $S$  in equation (17) with the use of a standard sample. However, in time-of-flight diffractometry advantage can be taken of the abundance of neutrons of short wavelength. As  $\lambda \rightarrow 0$ ,  $e^{-2W(\lambda)} \rightarrow 0$  and

$$y = S I(\lambda) A(\lambda) d\lambda \left( \sum_{\text{coh}} + \sum_{\text{incoh}} \right). \quad (18)$$

This method of determining an absolute scale eliminates errors related to the position of the specimen in the incident beam, differences in the time taken for each run, and intensity fluctuations in the beam. The total scattering cross sections are known and are independent of the physical state of the scatterer; hence  $S$  can be determined.

For diamond, which according to the 'International Tables for Crystallography' (Vol. 3) has a temperature factor  $B$  of  $0.20 \text{ \AA}^2$  ( $W = B \sin^2 \theta / \lambda^2$ ), only 1% of the intensity of a Bragg reflection remains at a wavelength of  $0.3 \text{ \AA}$  and a scattering angle of  $150^\circ$ .

## 5. Statistical Aspects of the Rietveld Method

The least-squares method used in the Rietveld procedure is standard; however, two topics require special mention.

### (a) Counting Statistics

It is assumed that the weights assigned to each profile point are given by

$$w_i = \text{var}^{-1}(y_i^{\text{obs}}).$$

This would be strictly true if the counts were normally distributed. However, as Price (1979) has pointed out, the observed count rate follows a Poisson distribution. In this case the weights should be assigned as

$$w_i = \text{var}^{-1}(y_i^{\text{calc}}).$$

The effect of the assumption of a normal distribution is to bias the calculated profile so that it is always slightly below the observed profile and the integrated intensity of the peak is underestimated. This conclusion was verified by Hewat and Sabine (1981) using computer simulated profiles.

The effect is serious only at very low count rates, and is very serious if the count is zero. Under normal conditions there are at least tens of counts at each profile point, and the systematic error introduced by using  $w_{ik} = \text{var}^{-1}(y^{\text{obs}})$  is small compared with the precision with which the peaks are measured.

### (b) Precision of Parameter Measurements

A controversy arose concerning the statistical justification of the Rietveld method. Sakata and Cooper (1979) concluded that the method was unsound because it gave lower standard deviations for the variable parameters when compared with an analysis of the same data using only integrated intensities. Hewat and Sabine (1981) showed that the two methods were identical when cognisance was taken of the fact that the integrated intensity was obtained from a profile.

In the Rietveld method the quantity

$$M_1 = \sum_i w_{ik} (y_{ik}^{\text{obs}} - y_{ik}^{\text{calc}})^2 \quad (19)$$

is minimised. The  $y_{ik}$  are defined by the relation  $y_{ik} = G_{ik} I_k$ , where  $G_{ik}$  is the profile function and  $I_k$  is the integrated intensity of the  $k$ th reflection. In the integrated intensity method  $M_2$  is minimised, where

$$M_2 = \sum_k W_k (I_k^{\text{obs}} - I_k^{\text{calc}}).$$

The condition that  $M_1 = M_2$  is

$$W_k = \sum_i G_{ik}^2 w_{ik}. \quad (20)$$

When the only values of integrated intensity available are the total areas under the diffraction peak, it is not difficult to show that (20) will hold only if the background intensity is zero. It was the existence of this result that led Sakata and Cooper (1979) to question the Rietveld procedure.

Hewat and Sabine (1981) showed that when knowledge of the profile function  $G_{ik}$  is incorporated into the determination of integrated intensities, each point on the profile gives a measure of the integrated intensity  $I_k^{(i)}$  through the relation

$$I_k^{(i)} = G_{ik}^{-1} y_{ik},$$

with variance given by

$$\text{var}(I_k^{(i)}) = G_{ik}^{-2} \text{var}(y_{ik}).$$

Evaluation of  $I_k$  as the weighted mean of  $I_k^{(i)}$  with weights equal to  $\text{var}(I_k^{(i)})$  leads directly to the general relation

$$W_k = \sum_i G_{ik}^2 w_{ik}.$$

This shows that, when the data are handled correctly, the results of a direct profile refinement and a refinement in which integrated intensities are evaluated as an intermediate step are identical.

**Table 1.** Values of the temperature factor  $B$  and the average edge length of a mosaic block  $D$  for MgO found by simultaneous Rietveld refinement of time-of-flight data at scattering angles of 90° and 150°

Parameter	Specimen			
	uM	2M	20M	50M
$B$ (Å <sup>2</sup> )	0.309(2)	0.302(2)	0.319(2)	0.322(2)
$D$ (μm)	0	0	8.7(5)	11.8(10)

## 6. Temperature Factors for Magnesium Oxide

As an example of the use of this formulation of the Rietveld method, Sabine *et al.* (1988) collected and analysed time-of-flight neutron data from four specimens of magnesium oxide. The specimens were those described by Sabine (1985). Data were collected at nominal scattering angles of 60°, 90° and 150° on the Special Environment Powder Diffractometer at Argonne National Laboratory. The nomenclature used in that work is followed here. The approximate average grain diameters were:

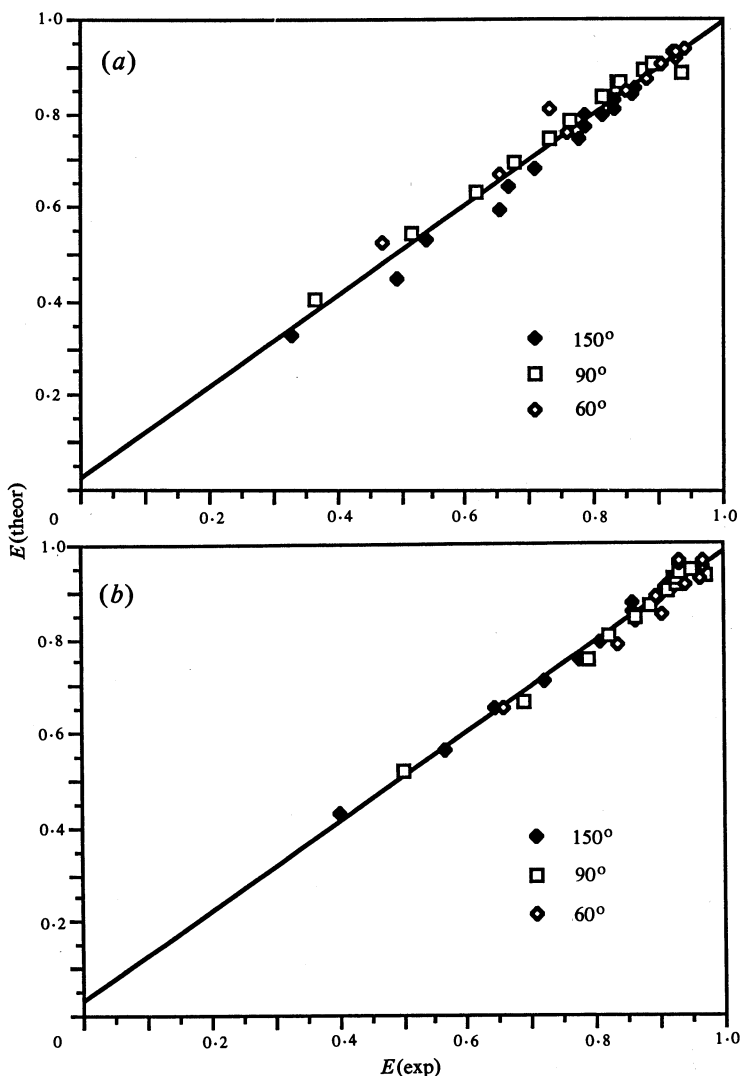
uM, 0.2 μm; 2M, 0.8 μm; 4M, 2 μm; 20M, 12 μm; 50M, 17 μm.

Earlier analysis using a version of the Rietveld program which did not contain provision for extinction had led to very low or negative values of  $B$  in specimens 20M and 50M. When equation (17) was used for  $y_i^{\text{calc}}$  the refinements converged satisfactorily giving the values of  $B$  and  $D$  shown in Table 1, where  $D$  is the edge length of a mosaic block which was assumed to be a cube.

To confirm that there was no interaction between the extinction parameter  $D$  and the other parameters in the refinement, which were the scale factor, the temperature factor, the zero point and diffractometer parameters, and the profile parameters, a separate determination of the experimental extinction factor was made. This was done

by normalising all data sets using the method given in equation (18). The integrated intensities from 2M and 4M, which agreed to 1% after normalisation, were assumed to represent  $I^{\text{kin}}$  in equation (8). For each reflection the mean integrated intensity of 2M and 4M was divided into the measured intensities from 20M and 50M to give  $E(\text{exp})$ . Equations were then used to calculate  $E(\text{theor})$  from the  $D$  values given by Rietveld refinement.

The results are given in Fig. 1. The agreement between the theoretical and experimental values of the extinction factor is excellent down to the most severe extinction condition found in the experiment.



**Fig. 1.** Experimental value of the extinction factor  $E(\text{exp})$  from a direct measurement of integrated intensities compared with extinction factors  $E(\text{theor})$  calculated from the results of Rietveld refinement: (a) 50M sample ( $D = 11.8 \mu\text{m}$ ) and (b) 20M sample ( $D = 8.7 \mu\text{m}$ ). Each point is a Bragg reflection. All data ( $60^\circ$ ,  $90^\circ$ ,  $150^\circ$ ) are used.

The experimental values of the temperature factor for MgO have been reviewed by Barron (1977), who found the best estimate of  $B = 0.314 \pm 0.01 \text{ \AA}^2$ . The average of the values given in Table 1 is  $0.313 \pm 0.01 \text{ \AA}^2$ .

## 7. Conclusions

It is possible to use the Rietveld method to obtain accurate values of crystallographic parameters from powder specimens even though dynamical effects reduce the intensity of strong reflections by a factor of three. While one would not choose specimens of high grain size, in many cases there is no choice. A study of Debye–Waller factors as a function of temperature has been a fruitful area of research. Any increase in extinction because of grain growth could completely nullify conclusions concerning the values of thermal vibration parameters. The extinction factor is temperature dependent through the  $F$  term in  $x$ , however the change is small compared with the effect of grain growth.

## Acknowledgments

I thank the Argonne National Laboratory, U.S.A. and the Rutherford–Appleton Laboratory, U.K. for providing me with the opportunity to become familiar with neutron time-of-flight methods.

## References

- Barron, T. H. K. (1977). *Acta Cryst. A* 33, 602–4.
- Darwin, C. G. (1922). *Philos. Mag.* 43, 800–29.
- Gurevich, I. I., and Tarasov, L. V. (1968). 'Low Energy Neutron Physics' (North Holland: Amsterdam).
- Hamilton, W. C. (1957). *Acta Cryst.* 10, 629–34.
- Hewat, A. W., and Sabine, T. M. (1981). *Aust. J. Phys.* 34, 707–12.
- Marshall, W., and Stuart, R. N. (1959). The scattering of neutrons from polycrystalline materials. UCRL-5568, Lawrence Radiation Laboratory.
- Price, P. F. (1979). *Acta Cryst. A* 35, 57–60.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.
- Sabine, T. M. (1980). *Aust. J. Phys.* 33, 565–72.
- Sabine, T. M. (1985). *Aust. J. Phys.* 38, 507–18.
- Sabine, T. M. (1988). *Acta Cryst.* (in press).
- Sabine, T. M., and Clarke, P. J. (1977). *J. Appl. Cryst.* 10, 277–80.
- Sabine, T. M., Von Dreele, R. B., and Jørgensen, J.-E. (1988). *Acta Cryst.* (in press).
- Sakata, M., and Cooper, M. T. (1979). *J. Appl. Cryst.* 12, 554–63.
- Zachariasen, W. H. (1945). 'Theory of X-ray Diffraction in Crystals' (Wiley: New York).