











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:

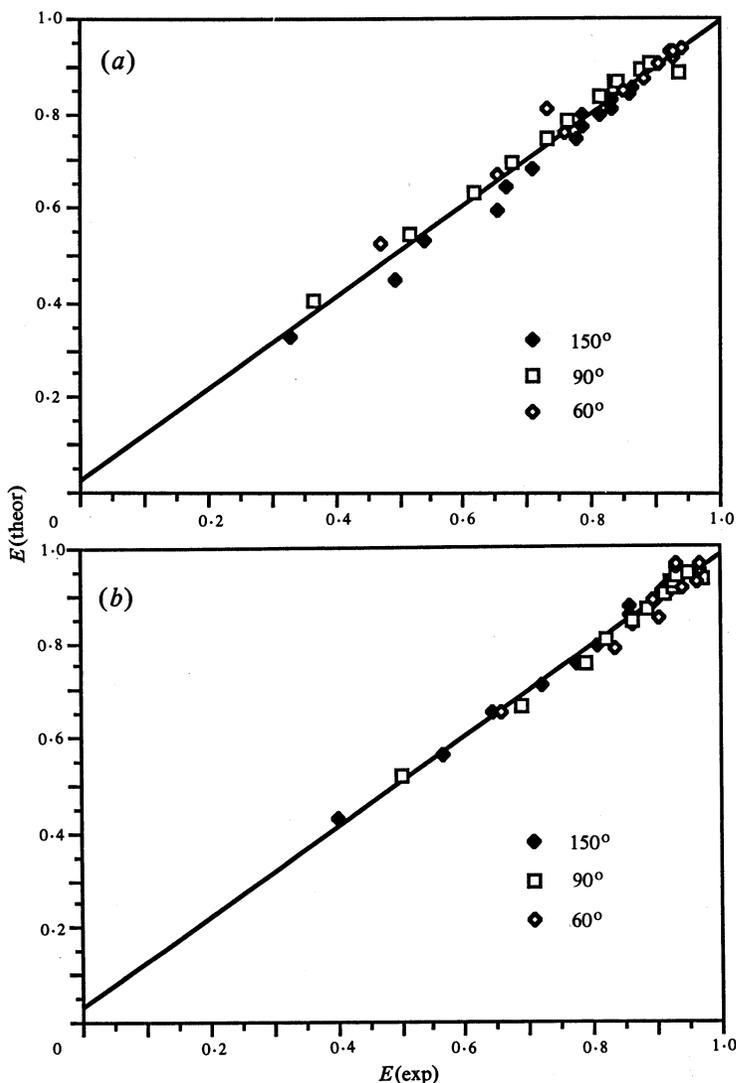
uM, 0.2 μm; 2M, 0.8 μm; 4M, 2 μm; 20M, 12 μm; 50M, 17 μm.

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.

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