8.6.2.4. *Preferred orientation and texture*

Preferred orientation is a formidable problem which can drastically affect the measured intensities. A simple correction formula for plate-like morphology was given by Rietveld (1969). Ahtee, Unonius, Nurmela & Suortti (1989) have shown how the effects of preferred orientation can be included in the refinement by expanding the orientation distribution in spherical harmonics. Quantitative texture analysis based on spherical harmonics has been implemented in the Rietveld refinement code by Von Dreele (1997). A general model of the texture has also been described by Popa (1992). It may be possible to remove or reduce the effect of preferred orientation by mixing the sample with a suitable diluent.

An additional problem is caused by particle size and strain broadening, which are not smooth functions of the diffraction angle. These effects can be taken into account by phenomenological models (*e.g.* Dinnebier *et al.*, 1999; Pratapa, O'Connor & Hunter, 2002) or by an analytical approach such as that of Popa & Balzar (2002).

The determination of the elastic stresses and strains in polycrystals can be determined from diffraction line shifts using Rietveld refinement (Popa & Balzar, 2001).

8.6.2.5. *Statistical validity*

Sakata & Cooper (1979) criticized the Rietveld method on the grounds that different residuals

$$y_i(\text{obs.}) - y_i(\text{calc.})$$

related to the same Bragg peak are correlated with one another, and they asserted that this correlation leads to an uncertainty in the standard uncertainties of the structural parameters. Prince (1981) has challenged this conclusion and stated that the s.u.'s given by the Rietveld procedure are correct if the crystallographic model adequately fits the data. However, even if the s.u.'s are correct, they are measures of precision rather than accuracy, and attempts to assess accuracy are hampered by lack of information concerning correlations between systematic errors (Prince, 1985, 1993).

references