3.5. Data reduction to $|F_{hkl}|$ values

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3.5.1. Introduction

Collecting the structure-factor amplitudes $|F_{hkl}|$ is the key step leading to structure solution from powder-diffraction data, just as from single-crystal data. However, there are specific difficulties and pitfalls associated with powder data, mainly because of diffraction-peak overlap. Once indexing is realized, data reduction to $|F_{hkl}|$ is a fast process, using whole-powder-pattern decomposition (WPPD) methods. This comfortable situation was not attained without past efforts, which are reviewed in this chapter. The introduction of modern WPPD methods occurred slowly and progressively over the past 30 years, thanks to increases in computer power, improvements in graphical user interfaces, diffractometer data digitalization, the availability of synchrotron and neutron radiation, and last but not least, the proposition of new algorithms. Innovations were not instantly accepted, this also being true for the Rietveld (1969) method, or could not be applied immediately to every type of powder data. Predecessors of the current WPPD methods extracted peak intensities without restraining the cell, so that each peak position was a parameter to be refined (as well as the peak intensity, and the peak shape and width). This is still useful if the aim is to obtain peak positions for indexing, although simple derivative methods can make searching for peak positions faster. Taking advantage of the indexing (Bergmann *et al.*, 2004), new WPPD methods that applied cell restraints to the peak positions opened the door to a long list of new possibilities and applications (including first indexing confirmation and manual or automatic space-group estimation) which are detailed in this chapter. A partial review of the applications realized in thousands of published papers is given, and the evolution of the methods will be discussed. Additional information on the topic of reduction to $|F_{hkl}|$ values can be found in the books by Young (1993), Giacovazzo (1998), David *et al.* (2002), Pecharsky & Zavalij (2003), Clearfield *et al.* (2008) and Dinnebier & Billinge (2008) or in selected reviews (Toraya, 1994; Langford & Louër, 1996; Le Bail, 2005).

3.5.2. Algorithms

Whole-powder-pattern fitting (WPPF) is a general definition including WPPD as well as the Rietveld method (Rietveld, 1969). In the latter method, the atomic coordinates are required for the intensity calculations, and the sum of all the peak contributions produces a calculated powder pattern which is compared to the observed one, allowing the least-squares refinement of profile and structural parameters. The Rietveld method historically preceded modern WPPD methods, though the latter are applicable without atomic coordinates. Of course, one may use WPPD methods if the structure is known, but in some cases one does not want to use that knowledge (not wanting to restrain the peak intensities by the structural model, for instance, nevertheless believing in the indexing or wanting to confirm it, using the restraint of the cell parameters). Any WPPF approach should be able to model the peak shape and width variations with diffraction angle (complications not considered here may occur in the case of anisotropic broadening intrinsic to the sample). This can be done by fitting some analytical profile shape and width parameters in a semi-empirical approach. The angular variation of these parameters is generally controlled by refining the U, V and W terms in the Caglioti *et al.* (1958) expression $[(\mathrm{FWHM})^2 = U\tan^2\theta + V\tan\theta + W]$ or a variation (where FWHM = full width at half maximum). The alternative is to use the fundamental parameter approach (FPA) (Cheary & Coelho, 1992). However, some of the original computer programs did not apply any cell restraint or even any restraint at all.

3.5.2.1. *Unrestrained cell*

Without a cell hypothesis, no $|F_{hkl}|$ values can be extracted; the intensity values collected will be noted by $I(i)$ until Miller indices are attributed, enabling the multiplicity correction. Obtaining all the peak positions, areas, breadths and shape parameters as independent values for a whole powder pattern is limited to simple cases where there is not too much peak overlap. With such an approach (both cell and space group unknown or unused) one has to estimate the number of peaks to be fitted, so that the fit of a complex group of peaks will lead to large uncertainties. However, knowing the cell and space group provides at least the correct number of peaks and an estimate of their starting positions. Such calculations were made as an alternative to the Rietveld method, during the first stage of the so-called two-stage method for refinement of crystal structures (Cooper *et al.*, 1981). In the case of X-ray data, the profile shapes applied in the Rietveld method (Gaussian at the beginning for neutron data) evolved a great deal (Wiles & Young, 1981), and on the WPPD side happened to be described in these two-stage approaches by a sum of Lorentzian curves, or double Gaussians (Will *et al.*, 1983, 1987). The computer program *PROFIT* (Scott, 1987), derived from software for individual profile fitting (Sonneveld & Visser, 1975) and extended to the whole pattern, was applied to the study of crystallite size and strain in zinc oxide (Langford *et al.*, 1986) and for the characterization of line broadening in copper oxide (Langford & Louër, 1991). Studying a whole pattern can also be done in simple cases by using software designed for the characterization of single or small groups of peaks; an example is a ZnO study (Langford *et al.*, 1993) using the computer program *FIT* (Socabim/Bruker). WPPD on complex cases is mostly realized today by using peak positions controlled by the cell parameters, with the benefit of stronger accuracy of the $|F_{hkl}|$ values, even if the lost degrees of freedom may lead to slightly worse fits, increasing the profile R factors. Before 1987, close to thirty structure determinations by powder diffractometry (SDPDs) were achieved using intensities extracted by using these old WPPD methods without cell constraints (see the SDPD database; Le Bail, 2007). It can be argued that freeing the peak positions allows one to take into account subtle effects in position displacement (in stressed samples, for example). But systematic discrepancy of observed peak positions with regard to the theoretical position, as expected from the cell parameters, can be modelled as well in modern WPPD methods or in the Rietveld method.

references