12.5–6 THE RIETVELD METHOD USING AN EXPERIMENTAL PROFILE CONVOLUTED BY ADJUSTABLE ANALYTICAL FUNCTION.

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The full potential of the Rietveld method as applied to the X-ray powder diffraction technique is not yet realized because of unsuccess of analytical peak-shape functions. It is shown that conventional Rwp value inferior to 10 % may be systematically obtained by a procedure combining the choice of an experimental profile for each compound and the refinement in shape and angular width variation of an analytical function convoluted with the former. Calculations are made with Fourier coefficients replacing the convolution by a more simple product ; for the choice of a standard $g(x)_{\theta 0}$ centered at θ_0 and defined between $-a/2$ and $a/2$, any reflexion $g(x, \theta)$ is obtained following the expression (for the even part) :

$$g(x, \theta) = \frac{1}{a} \sum_{-\infty}^{+\infty} A_n e^{-H_\theta^2 n^T} \cos \frac{2\pi nx}{a} ,$$

$$\text{where } A_n = \sum_{-\infty}^{+\infty} g(x)_{\theta 0} \cos \frac{2\pi nx}{a} ,$$

$$\text{and } H_\theta^2 = U (tg^2\theta - tg^2\theta_0) + V (tg\theta - tg\theta_0).$$

Corresponding sine coefficients are used for the odd part so that only two set of parameters U, V and T need to be refined. This procedure holds also for neutron powder data where T is obtained of the order of 2 (gaussian shape for the analytical part) compared to a value near 1 (cauchy shape) for the X-ray case. Applications have been made principally on fluoride compounds where Rwp of the order of 8 % (X-ray case, CuKα, $0<2\theta<150°$) are obtained when problems due to prefered orientation are solved (reflexion technique).

12.5–7 X-RAY RIETVELD STRUCTURE REFINEMENT INCORPORATING W*G DECONVOLUTION.

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Our previous studies (Adv. X-ray Anal. (1983) 26, 73) led us to fit X-ray powder diffraction profiles with a split Pearson VII function for each wavelength component (Kα 1, 2 and 3) using a Marquart refinement. Following the "Parrish Method" we have determined a set of profile standards defining W*G for our diffractometer and deconvoluted the specimen broadening profile S. The utilization of the convolution relation (F=W*G*S) in profile refinement procedures, reduces the complexity of the refinement by representing each profile with only the three sample related parameters: diffraction angle, intensity, and FWHM of the S profile. The broadening of the sample profiles, in this study, was successfully modeled with the Scherrer equation. For this case, only positions and intensities for each line, and a common parameter related to crystallite size, need be refined. We have extended these deconvolution procedures to the Rietveld crystal structure refinement technique. This method not only correctly fits the X-ray profiles but in addition eliminates the need to refine the U,V,W parameters associated with the profile breadth. Examples of calibration profile fitting and of Rietveld structure refinements with and without (W*G)*S deconvolution will be shown.

12.5–8 PEAK SHAPES AND HALFWIDTHS IN RIETVELD REFINEMENT OF POWDER DIFFRACTION DATA.

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A simple and physically intuitive model for the angular dependence of peak shapes and halfwidths for conventional and synchrotron x-ray data, and its application to Rietveld refinement is described. Both the instrumental resolution function and sample broadening effects are taken into account (see, for example, Wilson, "Mathematical Theory of X-ray Powder Diffractometry," (1963), Philips, Eindhoven; Klug and Alexander, "X-ray Diffraction Procedures," (1974), Wiley, New York; Langford, J. Appl. Cryst. (1978) 11, 10). In the case of Cu κα and κβ radiation, the instrumental resolution function for a diffractometer with typical focussing geometry is found to be well-represented by a convolution of Gaussian and Lorentzian functions for 2θ greater than about 40°. The Gaussian component contains contributions from the focal line, receiving slit and misalignment profiles, and the halfwidth (FWHM) Γ_G is found to be approximately constant, W, while the Lorentzian component represents the spectral profile and is found to have a halfwidth Γ_L roughly equal to $X\tan\theta$ (where $X = 2\Delta\lambda/\lambda \simeq 0.07°$ for Cu κβ). The convolution can be easily incorporated into standard Rietveld-type programs via the "pseudo-Voigt" approximation (Wertheim, Butler, West, and Buchanan, Rev. Sci. Instr. (1974) 11, 1369; Young and Wiles, J. Appl. Cryst. (1982) 15, 430) with simple polynomial functions of Γ_G and Γ_L and analytic expressions for the necessary derivatives. In the absence of sample broadening effects, Rietveld refinement of Cu κβ data can therefore be accomplished with only two variable profile-type parameters, W and X. Two additional parameters can be introduced if necessary to allow for particle size and strain broadening effects, with $1/\cos\theta$ and $\tan\theta$ dependences respectively.

This simple modification to the Rietveld program is also applicable to synchrotron x-ray and neutron powder diffraction data. In the latter case, the peak shapes are usually assumed to be purely Gaussian, but it is found that incorporation of a Lorentzian component leads to distinctly better fits in some cases. Such corrections will undoubtedly become more important in the next generation of high resolution neutron instruments.

The application of this model to a number of Rietveld refinements, including examples of Cu κβ, synchrotron and neutron diffraction data, will be described.

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