intensities of the derived profile parameters are normalized and stored in the computer for later use. Note that any change in the X-ray spectrum or instrument geometry requires another set of measurements. The instrument function is also an important aid in computer graphics as described in Subsection 2.3.3.9.

The fitting of conventional diffractometer profiles was considerably improved by the use of a convolution function, in which the Pearson VII function is convoluted with the observed instrument function (Toraya *et al.*, 1983; Toraya, 1988). Enzo, Fagherrazzi, Benedetti & Polizzi (1988; Benedetti, Fagherazzi, Enzo & Battagliarin, 1988) used the convolution of a pseudo-Voigt function as the true data function and the convolution of exponential and pseudo-Voigt functions as the instrumental function for crystallite size and strain analysis. These functions have advantages in analysing the crystallite size and strain, although they require longer computation time for calculating the convolution.

Background intensity is usually included in the refinement. A first- or second-order polynomial is used to represent the background function $B(x)$ in equation (2.3.3.12) in a small 2θ range, and the polynomial coefficients are adjusted during the least-squares refinement. In some cases, the background is subtracted from the pattern before the refinement by using the lowest intensities between the reflections. The background in the vicinity of high-intensity peaks and peak clusters is usually higher and should be avoided.

In the least-squares refinement, the following quantity is minimized:

$$\Delta = \sum_{i=1}^{N} w_i [Y(x_i)_{\rm obs} - Y(x_i)_{\rm calc}]^2, \qquad (2.3.3.17)$$

where N is the number of observations, w_i is the weight assigned to the ith observation, and $Y(x_i)_{\rm obs}$ is the observed profile intensity. A statistical weighting factor such as $w_i = \sigma_i^2$, where $\sigma_i^2 = 1/Y(x_i)_{\rm obs}$, is frequently used. The quality of the fitting procedure is generally expressed by R factors such as R_{wp}, the weighted R factor for profile intensity, which includes the entire scattering range and the background. The definitions of these factors are summarized by Young, Prince & Sparks (1982). The R_p and R_{wp} factors are given as

$$R_p(\%) = 100 \sum_{i=1}^{N} |Y(x_i)_{\rm obs} - Y(x_i)_{\rm calc}| \Big/ \sum_{i=1}^{N} Y(x_i)_{\rm obs}, \qquad (2.3.3.18)$$

$$R_{wp}(\%) = 100 \left\{ \frac{\sum_{i=1}^{N} w_i \left[Y(x_i)_{\rm obs} - Y(x_i)_{\rm calc} \right]^2}{\sum_{i=1}^{N} w_i Y(x_i)_{\rm obs}^2} \right\}^{1/2}. \qquad (2.3.3.19)$$

If the selected function is inappropriate, it will show up on the difference curve (experimental – calculated; see Fig. 2.3.3.9), and high R_p and R_{wp} factors.

A whole-powder-pattern fitting technique without using the structural model was proposed for analysing neutron powder data (Pawley, 1981) and then extended to X-ray data (Toraya, 1986). The method executes the whole pattern decomposition (*i.e.* fitting all the profiles) in one step. In this technique, the peak position T_j in equation (2.3.3.12) is a function of unit-cell parameters, and the unit-cell parameters are refined instead of individual peak positions. Furthermore, the angular dependence of the profile width can be expressed approximately as

$$w(2\theta) = \sqrt{w_1 + w_2 \tan\theta + w_3 \tan^2\theta}, \qquad (2.3.3.20)$$

where w_1, w_2, and w_3 are adjustable parameters (Caglioti, Paoletti & Ricci, 1958); but see also Louër & Langford (1988). The profile-shape dependency on 2θ is ignored when fitting a small 2θ range, but it must be taken into account in the whole-powder-pattern fitting in both focusing and parallel-beam geometries. The least-squares ill conditioning is handled by imposing the constraints on the peak positions in the profile-fitting procedure.

Approximate unit-cell parameters are required to start the refinement. Advantages of this technique are: (1) the unit-cell parameters are refined to high precision; (2) the analysis is rapid and straightforward; (3) it is also powerful in analysing complex powder patterns. The output of indices and integrated intensities of all reflections can be used to calculate Patterson and Fourier diagrams, and thus used for *ab initio* structure determination (McCusker, 1988) and the structure refinement based on the integrated intensities such as used in the *POWLS* program (Will, 1979).

The convolution equation is used in place of $P(x)$ in equation (2.3.3.12), in which the true data function represented by a pseudo-Voigt or Pearson VII has adjustable parameters of crystallite size and strain (Toraya, 1989). The anisotropic crystallite size assuming cylindrical shape has been determined by whole-powder-pattern fitting for complex powder patterns.

The advantage of profile fitting is illustrated in Fig. 2.3.3.10 for the quartz cluster at 68° with Cu $K\alpha$ where the doublet separation is 0.19° and the FWHM is 0.14°. The relative intensities of the 122, 203, and 301 $K\alpha_1$ peaks are 81:97:100, which differ from the profile-fitted peaks, 90:100:67, due to the overlapping. The sum of the fitted curves is the solid line which passes through the experimental points. The peak-search (or strip-chart) intensities that are not corrected for overlaps are more likely to correspond to the ICDD powder file than the profile-fitted values. Profile fitting is capable of about $\pm 0.0004°2\theta$ and 0.2% intensity for good experimental data (Parrish & Huang, 1980). Even in data with poor counting

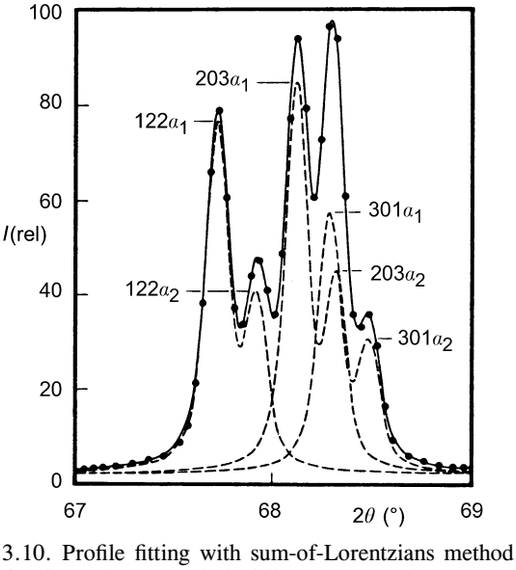

Fig. 2.3.3.10. Profile fitting with sum-of-Lorentzians method. Individual reflections shown as dashed-line curves and sum as solid line passing through experimental points. Quartz peak cluster, Cu $K\alpha_1$, $K\alpha_2$, conventional diffractomer.

references