3.5.2.2. *Restrained cell*

WPPD methods that strictly applied the peak positions calculated from a cell (hypothesized from indexing results) marked a great step forward in the quest for improving the SDPD success rate. This is essentially because the quality of the estimated intensities increased, and even if the main handicap of powder diffraction (peak overlap) could not be completely circumvented, it was at least more clearly delimited. Today two generic names are retained for such cell-restrained WPPD methods that can produce a set of extracted $|F_{hkl}|$ values suitable for attempting a structure solution: the Pawley and Le Bail methods. Both were derived from the Rietveld (1969) method, so they share with it many equations which will not be restated here (see Chapter 4.7).

3.5.2.2.1. *Pawley method*

The idea of removing the crystal structure refinement part in a Rietveld program and adding the potential to refine an individual intensity for every expected Bragg peak produced a new software package (named *ALLHKL*) allowing refinement of the cell parameters very precisely and extraction of a set of structure-factor amplitudes (Pawley, 1981). The process was much later called the 'Pawley method'. Overcoming the least-squares ill conditioning due to peak overlap was achieved by using slack constraints (Waser, 1963). Pawley clearly insisted on the usefulness of the procedure for the confirmation of the indexing of a powder pattern of an unknown. Nevertheless, the structure of the C_6F_{10} (at 4.2 K) test case selected for demonstration purposes remained unsolved (but see Section 3.5.4.2 below). No SDPD of an unknown was realized using the Pawley method for several years (although successful tests were published corresponding to redeterminations of previously known structures). The first real SDPD of an unknown using the Pawley method seems to be that of I_2O_4 (Lehmann *et al.*, 1987); its powder pattern had been previously indexed, but the structure not determined because of the lack of a suitable single crystal. During these pioneering years, *ALLHKL* could not extract the intensities for more than 300 peaks, so that, in more complex cases, it was necessary to subdivide the pattern into several parts. Moreover, it was rather difficult to avoid completely the ill conditioning due to overlapping peaks. Successful fits yielded equipartitioned intensities (*i.e.*, equal structure factors for those Bragg peaks with exact overlap). Unsuccessful fits could easily produce negative intensities which, combined with positive ones for other peak(s) at the same angle, reproduced the global positive value. Moreover, the first version to apply Gaussian peak shapes could not easily produce any SDPD because of the relatively poor resolution of constant-wavelength neutron data, so that it needed to be adapted to X-ray data, with the implementation of more complex peak shapes. Several programs were subsequently developed, based on the same principles as the original Pawley method. The first of them, by Toraya (1986), extended the use to X-ray data with non-Gaussian profile shapes, and introduced two narrow band matrices instead of a large triangular matrix, saving both computation time and memory space in a program named *WPPF*. Some programs were used to produce intensities in order to apply the so-called two-stage method (Cooper *et al.*, 1981) for structure refinement, such as *PROFIT* (Scott, 1987) and *PROFIN* (Will, 1988) (no slack constraints, but equal division of the intensity between expected peaks when the overlap was severe). There was intense continuing activity on Pawley-like software with other programs such as *FULFIT* (Jansen *et al.*, 1988), *LSQPROF* (Jansen *et al.*, 1992) and *POLISH* (Byrom & Lucas, 1993). Estimation of intensities of overlapping reflections was improved in *LSQPROF* by applying relations between structure-factor amplitudes derived from direct methods, and the Patterson function was considered in the satellite program *DOREES* (Jansen *et al.*, 1992). The question of how to determine the intensities of completely (or largely) overlapping reflections (either systematic overlap due to symmetry or fortuitous overlap) from a single powder pattern cannot have a definite simple answer, but continues to be discussed, since it is essential for improving our ability to solve structures. An early view with a probabilistic approach was given by David (1987), later introducing Bayesian statistics (Sivia & David, 1994) into the Pawley method. Early detection of preferred orientation on the basis of analysis of the *E*-value distribution was another way (Peschar *et al.*, 1995) to improve the structure-factor-amplitude estimate. New computer programs based on the Pawley method continue to be written even today.

3.5.2.2.2. *Le Bail method*

In order to be able to estimate *R* factors related to integrated intensities, Rietveld (1969) stated [see also the book *The Rietveld Method* edited by Young (1993)]: 'a fair approximation to the observed integrated intensities can be made by separating the peaks according to the calculated values of the integrated intensities,' *i.e.*

$$I_{hkl}(\text{obs}) = \sum_j [w_{j,hkl} S^2_{hkl}(\text{calc}) y_j(\text{obs})/y_j(\text{calc})], \qquad (3.5.1)$$

where $w_{j,hkl}$ is a measure of the contribution of the Bragg peak at position $2\theta_{hkl}$ to the diffraction profile y_j at position $2\theta_j$ [corresponding to equation 7 in Rietveld (1969)]. S^2_{hkl} is the sum of the nuclear and magnetic contributions for neutron diffraction, or is more simply F^2_{hkl} for X-rays. The sum is over all y_j(obs) that can theoretically contribute to the integrated intensity I_{hkl}(obs). Bias is introduced here by apportioning the intensities according to the calculated intensities; this is why the observed intensities are said to be 'observed', in quotation marks, in the Rietveld method. These 'observed' intensities are used in the R_B and R_F calculations (residuals on intensities and structure-factor amplitudes, respectively). They are also required for Fourier-map estimations, which, as a consequence, are less reliable than those from single-crystal data.

A process using the Rietveld decomposition formula iteratively for WPPD purposes was first applied in 1988 (Le Bail *et al.*, 1988) and much later was called the 'Le Bail method' or 'Le Bail fit', or 'pattern matching' as well as 'profile matching' in the *FULLPROF* Rietveld program (Rodriguez-Carvajal, 1990). In the original computer program (named *ARITB*), arbitrarily all equal S^2_{hkl}(calc) values are first entered in the above equation, instead of using structure factors calculated from the atomic coordinates, resulting in 'I_{hkl}(obs)' which are then re-entered as new S^2_{hkl}(calc) values at the next iteration, while the usual profile and cell parameters (but not the scale) are refined by least squares (*ARITB* used profile shapes represented by Fourier series, either analytical or learned from experimental data, providing an easy way to realize convolution by broadening functions modelling size–strain sample effects, possibly anisotropic). Equipartition of exactly overlapping reflections comes from the strictly equal result from equation (3.5.1) for Bragg peaks at the same angles which would have equal starting calculated intensities. Not starting from a set of all equal S^2_{hkl}(calc) values avoids equipartition for the exactly overlapping reflections but produces I_{hkl}(obs) keeping the same original ratio