through several generations, with the aim of generating sets of possible trial cell parameters.

(2) The search procedure, using a GA, is performed in restricted, sensible cell-volume ranges consistent with the knowledge of the system under study.

(3) For each set of trial parameters a calculated powder diffraction pattern is constructed. The peak positions and parameters describing the shape and width of each peak are used in the Le Bail profile-fitting procedure (Chapter 3.5).

(4) The pattern is split into different regions (defined by the user), and the weighted profile R factor is calculated for each region; all the values are summed to obtain the overall $R'_{\rm wp}$:

$$R'_{\rm wp} = \sum_{\rm regions} \left[\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i w_i y_i^2} \right]^{1/2},$$

where the summation is over the regions, i runs over the experimental points belonging to each region and y_i and y_{ci} are the observed and calculated profile at the ith experimental step, respectively. *Via* the $R'_{\rm wp}$ formula the residual for each region is scaled according to the total intensity in the region, so a region with only low-intensity peaks can make an important contribution to $R'_{\rm wp}$.

This approach is robust at handling the problems that may affect the experimental powder pattern: peak overlap, (hkl)-dependent effects and zero-point errors. It is time consuming (particularly in the case of low symmetry) but not very sensitive to the presence of minority impurity phases.

3.4.4.3.3. *McMaille: indexing via a Monte Carlo search method*

The information in the whole powder diffraction profile is exploited by the program *McMaille* (Le Bail, 2004), which is based on the random generation of cell parameters and uses the Monte Carlo optimization technique. Once the trial cell parameters have been generated and the Miller indices and the peak positions have been calculated, the quality of the cell is assessed by using, as figure of merit, the conventional Rietveld profile reliability factor R_p (Young, 1993) or McM_{20} (see Section 3.4.2.1). The program uses some tricks that can increase the success of the Monte Carlo algorithm:

(1) Only the trial cells corresponding to a value of R_p that is smaller than a user-defined value (∼50%) are retained for successive refinement.

(2) If all the observed peaks, except for a user-defined number of tolerated impurity peaks, are 'explained' whatever the R_p value, the cell is retained for successive examination.

(3) If either of the conditions (1) or (2) is fulfilled, the cell parameters are randomly changed in 200 to 5000 attempts (for cubic to triclinic cases, respectively) in which small random parameter variations *via* the Monte Carlo algorithm are carried out. The new parameters are preserved if an improvement of R_p is verified in 85% of the attempts.

This procedure is not sensitive to impurity lines, provided that the sum of their intensities is less than 10–15% of the total intensity. A zero-point error up to 0.05° is tolerated. To reduce the long computing time required to successfully complete the procedure, a significant increase in speed has been obtained by using idealized profiles generated by applying simplified line profiles to extracted line positions. A parallelized version of *McMaille* has also been developed. The indexing problem can usually be solved in few minutes if: (*a*) no triclinic symmetry is handled (because this requires more computing time); (*b*) the cell volume is less than 2000 Å^3; (*c*) no cell length is longer than 20 Å.

3.4.4.4. *Crysfire: a suite of indexing programs*

The *Crysfire* suite (Shirley, 2002) is a multi-program indexing facility. It can perform a self-calibration, which is aimed at detecting and correcting 2θ zero errors, and is able to strip out weak lines. Its single unified user interface and data-file format make a wide set of indexing packages accessible with minimal effort (especially to non-specialists). *Crysfire* provides a list of the possible cells suggested by each indexing program, suitably ranked. The *Crysfire* 2003 suite supports a total of 11 programs (Bergmann *et al.*, 2004), among which are *ITO*, *TREOR90*, *DICVOL91* and *McMaille*. The possibility of using different indexing programs, working in parameter space or index space and adopting different indexing approaches increases the probability of finding the correct cell.

3.4.4.5. *Two commercial programs*

3.4.4.5.1. *SVD-Index*

This commercial indexing program (Coelho, 2003*a*), which uses the Monte Carlo method, is part of the *TOPAS* (Coelho, 2003*b*) suite from Bruker AXS. The reciprocal-cell parameters in equation (3.4.2) are found by using, in an iterative way, the singular value decomposition (SVD) approach (Nash, 1990) to solve linear equations relating (hkl) values to d spacings. The method is particularly useful in cases for which there are more equations than variables. All the observed lines in the powder pattern are involved in the indexing procedure. It is claimed that the program is relatively insensitive to impurity peaks and missing high d spacings; it performs well on data with large diffractometer zero errors.

More recently, two indexing methods have been introduced in *TOPAS*: LSI (least-squares iteration), an iterative least-squares process which operates on the d-spacing values extracted from reasonable-quality powder diffraction data, and LP-Search (lattice parameter search), a Monte Carlo based whole-powder-pattern decomposition approach independent of the knowledge of the d-spacings (Coelho & Kern, 2005).

3.4.4.5.2. *X-CELL*

This commercial program is part of the *Materials Studio* suite from Accelrys (Neumann, 2003). To perform an exhaustive search, like *DICVOL*, the program uses the successive-dichotomy approach. Its principal features are:

(1) the user can define how many impurity lines can be tolerated;

(2) a search for the zero-point shift of the diffraction pattern; and

(3) systematic absences are taken into account.

The program is described as 'virtually exhaustive'; it is expected to work well when faced with missing lines, impurities and errors.

3.4.4.6. *Examples of applications of indexing programs*

3.4.4.6.1. *Indexing using DICVOL06*

The program *DICVOL06*, as implemented in the *WinPLOTR*/*FULLPROF* suite (Roisnel & Rodríquez-Carvajal, 2001) and recently introduced into *EXPO*, was applied to two experimental diffraction patterns.

Example 1

Norbornene (Brunelli *et al.*, 2001). Published information: C_7H_{10}, monoclinic, a = 7.6063 (9), b = 8.6220 (1), c = 8.749 (1) Å, β = 97.24 (1)°, $P2_1/c$, experimental range 5–60° 2θ, λ = 0.85041 Å, RES = 1.0 Å (where RES is the data resolution), synchrotron data, indexed by *Fzon* (Visser, 1969).