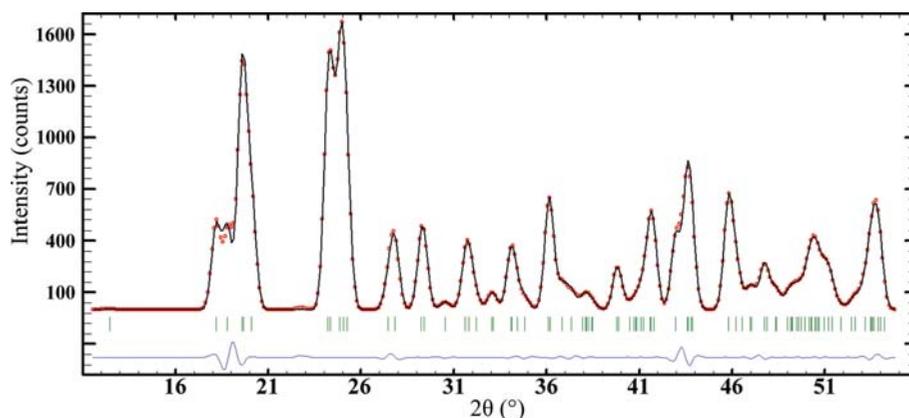
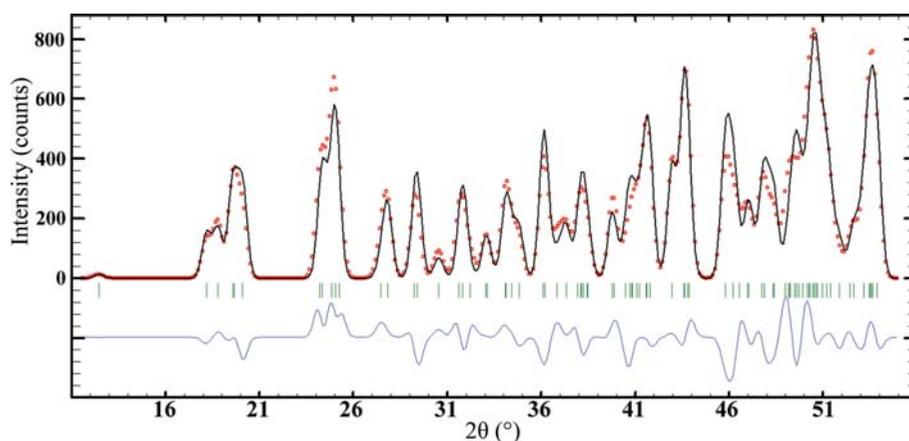


3.5. DATA REDUCTION TO $|F_{hkl}|$ VALUES**Figure 3.5.1**

Data reduction to $|F_{hkl}|$ values for the C_6F_{10} Pawley (1981) test case by the Le Bail method using *FULLPROF*. The neutron powder pattern (4.2 K) was rebuilt ($\lambda = 1.909 \text{ \AA}$) from the intensities given in the original paper ($P2_1/m$). The extraction of $|F_{hkl}|$ values was carried out in the space group $P2_1/n$.

**Figure 3.5.2**

The C_6F_{10} Monte Carlo molecule positioning by the real-space *ESPOIR* program produces that best fit ($R_p = 13.6\%$) of the pseudo powder pattern built from the previously extracted $|F_{hkl}|$ values (Fig. 3.5.1), overcoming the equipartition problem at the reduction stage. Compared to Fig. 3.5.1, which shows intensities, the multiplicity and geometrical factors are removed, leading to structure-factor amplitudes.

3.5.3.3. Background-estimation effects

Logically, a background value will never be higher than the observed intensity at the diffraction angle where it is visually estimated. In the first refinement cycles by the Pawley or Le Bail methods, it is preferable to keep the background fixed as well as the cell parameters, which assumes that the starting values have been carefully estimated or even (in the cell-parameter case) have already been refined from the peak positions that were used for indexing. This is because all refinement processes need to start from parameters close to the final values. Selecting background values leading to negative intensities after background removal could result in negative $|F_{hkl}|$ values if the software does not account for this.

3.5.4. Applications and by-products

The first modern WPPD method with cell restraints was developed for neutron data by Pawley (1981), 12 years after the publication of the paper that described the Rietveld (1969) method. In Le Bail *et al.* (1988) a new WPPD approach was used to extract intensities, making use of iterations of the Rietveld decomposition formula. It is clear that both these WPPD methods are children of the Rietveld method. Today most users of the Rietveld method do not cite the original Rietveld papers,

but only refer to the computer program that they used. This is also now increasingly the case for the WPPD methods.

From the Thomson Reuters ISI citation index consulted in May 2015, the papers for the Pawley and Le Bail methods scored 892 and 1425 direct citations, respectively. There are several highly cited papers that then cite these two papers. The most highly cited paper (>5100 times) that cites both WPPD methods concerns use of the Le Bail intensity-extraction method by Rodriguez-Carvajal, 1993). This paper is also given as a reference for *FULLPROF* used in more standard Rietveld refinements. This suggests that the impact of WPPD methods is higher than commonly believed. The list of possible WPPD applications includes phase identification, quantitative phase analysis, measurement of crystallite sizes and strains, creation of Fourier maps for partially solved structures, structure refinement by the two-step method, studies of electron-density distribution, and characterization of pole figures, using either the Pawley or Le Bail methods. All routes to SDPD use at least one of them. WPPD has even entered into the indexing step, with Kariuki *et al.* (1999) using the Le Bail fit for testing cell hypotheses (for which it is faster than the Pawley method) in a new computer program that uses a genetic algorithm. But the main applications of the WPPD methods are to provide support for cell-parameter refinement and the determination of the space group, as a

3. METHODOLOGY

prelude to the full use of the extracted $|F_{hkl}|$ values for *ab initio* structure solution.

3.5.4.1. Supporting indexing and space-group determination

As they yield the smallest possible profile R_p and R_{wp} factors (smaller than from the Rietveld method, which is limited by the crystal-structure refinement), the Pawley and Le Bail methods provide strong support for both the proposed indexing and the determination of the space group. Some computer programs provide an automated suggestion for the latter. This support is needed to show that it is worth attempting to solve the structure. Once the structure is solved, the structure constraint will remove the ambiguity between intensities of close Bragg peaks and necessarily improve the quality of the cell parameters. If the structure is already known, the best approach is the Rietveld method. There is a progression in the precision of the refined cell parameters from the lowest level (least squares from individually extracted peak positions) to a medium level (WPPD with cell restraint) to the highest possible level (Rietveld, adding the structure constraint). With both Pawley and Le Bail methods, the fit quality is checked using agreement factors which are the same as with the Rietveld method: R_p and R_{wp} (moreover, a careful visual check is recommended). The reliabilities relative to the structure (R_B and R_F), which can still be calculated, are meaningless (WPPD programs tending to obtain a value close to zero for both of them).

3.5.4.2. Structure solution

SDPD can be undertaken by various approaches, depending on the chemical knowledge of the sample (formula, molecular formula, presence of defined polyhedra . . .), either directly using the $|F_{hkl}|$ values for structure solution by direct or Patterson methods, or by rebuilding a pseudo powder pattern from them, or by applying fixed profile parameters from the Pawley or Le Bail fits during whole-powder-pattern fitting wherein the structure solution is attempted by real-space methods. In order to illustrate the power of WPPD methods and to show the progress realized over the last 30 years, the decafluorocyclohexene structure that was unsolved in the Pawley method paper of 1981 is reconsidered. As stated by Pawley, from plausible extinctions the space group of the C_6F_{10} crystal structure at 4.2 K could well be $P2_1/n$. The $|F_{hkl}|$ values were extracted from the rebuilt neutron powder pattern by applying the Le Bail method and used for attempting the structure solution by real-space methods. The neutron

powder pattern was rebuilt from the 109 intensities extracted up to $54^\circ 2\theta$, in space group $P2_1/n$, given in Table 2 of the original paper. The fit (using *FULLPROF*) in $P2_1/n$ of the data rebuilt in $P2_1/n$ is satisfactory (Fig. 3.5.1). The three-dimensional C_6F_{10} molecule was rotated and translated (six degrees of freedom) in the cell using the *ESPOIR* (Le Bail, 2001) Monte Carlo program, leading to a plausible starting model ($R_p = 13.6\%$) ready for Rietveld refinement. This program builds a pseudo powder pattern from the extracted $|F_{hkl}|$ values, which is then compared to the data calculated from the model (Fig. 3.5.2). Unrefined atomic coordinates are available from the Crystallography Open Database (COD, CIF No. 3500009) (Grazulis *et al.*, 2009); a projection of the corresponding structure is shown in Fig. 3.5.3. The true crystal structure is apparently more complex (Solovyov *et al.*, 2014). Final resolution of the structure will require collection of a better experimental powder pattern. However, the coordinates have been refined by energy minimization in the solid state (Smrčok *et al.*, 2013).

3.5.5. Conclusion

‘Which is best: the Pawley or the Le Bail method?’ is not a question with a simple conclusive answer. The fact is that both methods are able to estimate structure-factor amplitudes, which can lead to structure solution from powder-diffraction data in a more efficient way than was previously possible, even if the problem of peak overlap precludes attaining single-crystal quality data from only one powder pattern. The advantage of the Le Bail method over the Pawley method is its speed, which becomes apparent when several thousands of $|F_{hkl}|$ values have to be extracted, for instance from high-resolution synchrotron data of a complex compound, since no more than about ten parameters have to be refined instead of thousands. Chemical knowledge may reduce the number of $|F_{hkl}|$ values necessary for solving a structure to the first 100 Bragg peaks at low diffraction angles, as shown in the above example. Moreover, the small number of successful participants in the three SDPD round robins held in 1998, 2002 and 2008 (Le Bail *et al.*, 2009) did not allow us to conclude whether one approach is really better than the other, or even to be sure if all the further modifications of the extracted $|F_{hkl}|$ values in particular computer programs are really decisive improvements (the conclusion was that SDPD ‘on demand’ was still not an easy task). WPPD is not the only reef on the SDPD journey; indexing remains a considerable bottleneck for complex materials and low-resolution data.

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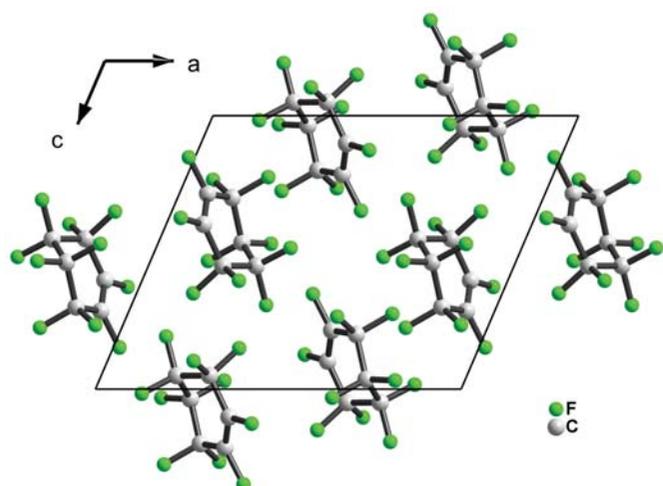


Figure 3.5.3
Projection along the b axis of the C_6F_{10} structure model in $P2_1/n$ before Rietveld refinement.