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° 2θ, in space group $P2/m$, given in Table 2 of the original paper. The fit (using *FULLPROF*) in $P2_1/n$ of the data rebuilt in $P2/m$ 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).

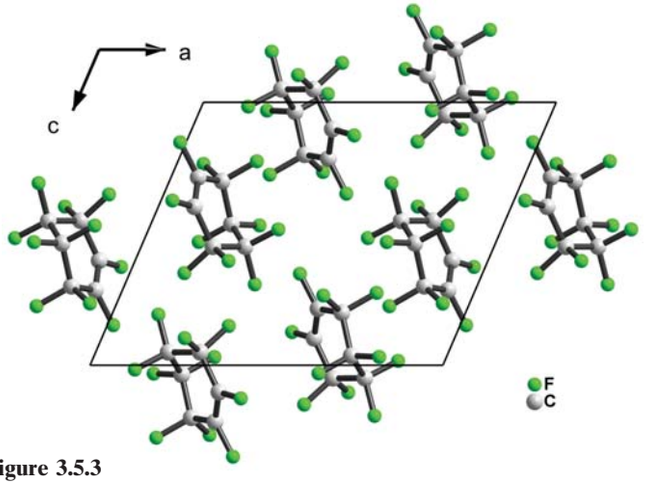

Figure 3.5.3
Projection along the *b* axis of the C_6F_{10} structure model in $P2_1/n$ before Rietveld refinement.

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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