

3. METHODOLOGY

FOMnew in *N-TREOR09*). The first one in the list is the correct cell. It is worth mentioning that the classical M_{20} figure of merit was not able to pick up the solution. The best cell parameters, found according to FOMnew, were $a = 24.0951$ (50), $b = 6.1697$ (21), $c = 12.4578$ (37) Å, $\beta = 102.724$ (18)°, similar to those reported in the literature, with FOMnew = 0.61, $M_{20} = 12$; all the lines in the pattern were indexed. The program provided the solution thanks to its automatic check for a zero-point correction (2θ zero shift = 0.04°) and was able to correctly identify the extinction group (I_a). For the second suggested cell (the wrong solution) FOMnew = 0.41, $M_{20} = 15$, and two lines were unindexed.

Example 4

Hexagonal turkey egg-white lysozyme (Margiolaki *et al.*, 2005). Published information: hexagonal, $a = 71.0862$ (3), $c = 85.0276$ (5) Å, $P6_122$, experimental range 0.4–12° 2θ , RES = 3.35 Å, synchrotron data. The first 94 peaks (in the range 0.4–6°, $\lambda = 0.700667$ Å) with intensities greater than a default threshold were selected. An intensity-based criterion was automatically adopted. The first 25 lines were used to find possible cells that were then refined by considering all 94 peaks. Five possible unit cells were automatically suggested by the program in the following systems: hexagonal (1), orthorhombic (1) and monoclinic (3). The highest value for WRIP20 was 0.99, and was for the correct hexagonal cell parameters: $a = 71.0922$ (4), $c = 85.0269$ (7) Å, which are similar to those reported in the literature; all the 94 selected lines in the pattern were indexed. For this cell, the program detected a geometrical ambiguity (see Section 3.4.2.2) between hexagonal and orthorhombic lattices and automatically selected the higher-symmetry one.

3.4.5. Conclusion

Indexing a powder diffraction pattern is sometimes described as a 'gateway technology', because the determination of the cell parameters is so fundamental: if no cell has been identified the execution of the subsequent steps of the structure solution process is impossible, and if a wrong cell has been used the correct solution is unreachable. Therefore extremely close attention must be paid to the indexing step of the process. From the early 1970s, the increasing interest in powder pattern indexing and the progress seen, in terms of both methods and algorithms, have strongly contributed to opening the door to modern applications of powder diffraction techniques. The availability of a quite large number of software packages, based on different indexing strategies, enables the scientist interested in solving crystal structures to switch from one program to another when the first fails, so increasing the possibility of success. In some cases indexing is still a challenging process. Good-quality data are necessary and careful inspection of each indexing step, in particular in the selection of the experimental peak positions to be used, is advisable.

References

- Altomare, A., Caliandro, R., Camalli, M., Cuocci, C., da Silva, I., Giacovazzo, C., Moliterni, A. G. G. & Spagna, R. (2004). *Space-group determination from powder diffraction data: a probabilistic approach*. *J. Appl. Cryst.* **37**, 957–966.
- Altomare, A., Camalli, M., Cuocci, C., da Silva, I., Giacovazzo, C., Moliterni, A. G. G. & Rizzi, R. (2005). *Space group determination: improvements in EXPO2004*. *J. Appl. Cryst.* **38**, 760–767.
- Altomare, A., Campi, G., Cuocci, C., Eriksson, L., Giacovazzo, C., Moliterni, A., Rizzi, R. & Werner, P.-E. (2009). *Advances in powder diffraction pattern indexing: N-TREOR09*. *J. Appl. Cryst.* **42**, 768–775.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Burla, M. C. & Polidori, G. (1995). *On the number of statistically independent observations in a powder diffraction pattern*. *J. Appl. Cryst.* **28**, 738–744.
- Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N. & Falcicchio, A. (2013). *EXPO2013: a kit of tools for phasing crystal structures from powder data*. *J. Appl. Cryst.* **46**, 1231–1235.
- Altomare, A., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Rizzi, R. & Werner, P.-E. (2000). *New techniques for indexing: N-TREOR in EXPO*. *J. Appl. Cryst.* **33**, 1180–1186.
- Altomare, A., Giacovazzo, C. & Moliterni, A. (2008). *Indexing and space group determination*. In *Powder Diffraction Theory and Practice*, edited by R. E. Dinnebier & S. J. L. Billinge, pp. 206–226. Cambridge: RSC Publishing.
- Andrews, L. C. & Bernstein, H. J. (1988). *Lattices and reduced cells as points in 6-space and selection of Bravais lattice type by projections*. *Acta Cryst.* **A44**, 1009–1018.
- Banerjee, S., Mukherjee, A., Neumann, M. A. & Louër, D. (2002). *Ab-initio structure determination of a Cu(II)-Schiff base complex from X-ray powder diffraction data*. *Acta Cryst.* **A58**, c264.
- Bergmann, J. (2007). *EFLECH/INDEX – another try of whole pattern indexing*. *Z. Kristallogr. Suppl.* **26**, 197–202.
- Bergmann, J., Le Bail, A., Shirley, R. & Zlokazov, V. (2004). *Renewed interest in powder diffraction data indexing*. *Z. Kristallogr.* **219**, 783–790.
- Boultif, A. & Louër, D. (1991). *Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method*. *J. Appl. Cryst.* **24**, 987–993.
- Boultif, A. & Louër, D. (2004). *Powder pattern indexing with the dichotomy method*. *J. Appl. Cryst.* **37**, 724–731.
- Brunelli, M., Fitch, A. N., Jouanneaux, A. & Mora, A. J. (2001). *Crystal and molecular structures of norbornene*. *Z. Kristallogr.* **216**, 51–55.
- Buerger, M. J. (1957). *Reduced cells*. *Z. Kristallogr.* **109**, 42–60.
- Buerger, M. J. (1960). *Note on reduced cells*. *Z. Kristallogr.* **113**, 52–56.
- Coelho, A. A. (2003a). *Indexing of powder diffraction patterns by iterative use of singular value decomposition*. *J. Appl. Cryst.* **36**, 86–95.
- Coelho, A. A. (2003b). *TOPAS. Version 3.1 User's Manual*. Bruker AXS GmbH, Karlsruhe, Germany.
- Coelho, A. A. & Kern, A. (2005). *Discussion of the indexing algorithms within TOPAS*. *IUCr Commission on Powder Diffraction Newsletter*, **32**, 43–45.
- Conway, J. H. & Fung, F. Y. C. (1997). *The Sensual (Quadratic) Form*. Washington, DC: The Mathematical Association of America.
- Delaunay, B. (1933). *Neue Darstellung der geometrischen Kristallographie*. *Z. Kristallogr.* **84**, 109–149.
- Dong, C., Wu, F. & Chen, H. (1999). *Correction of zero shift in powder diffraction patterns using the reflection-pair method*. *J. Appl. Cryst.* **32**, 850–853.
- Giacovazzo, C. (2011). *Crystallographic computing*. In *Fundamentals of Crystallography*, 3rd ed., edited by C. Giacovazzo, pp. 66–156. Oxford: IUCr/Oxford University Press.
- Harris, K. D. M., Johnston, R. L., Chao, M. H., Kariuki, B. M., Tedesco, E. & Turner, G. W. (2000). *Genetic algorithm for indexing powder diffraction data*. University of Birmingham, UK.
- Ishida, T. & Watanabe, Y. (1967). *Probability computer method of determining the lattice parameters from powder diffraction data*. *J. Phys. Soc. Jpn*, **23**, 556–565.
- Ishida, T. & Watanabe, Y. (1971). *Analysis of powder diffraction patterns of monoclinic and triclinic crystals*. *J. Appl. Cryst.* **4**, 311–316.
- Ito, T. (1949). *A general powder X-ray photography*. *Nature*, **164**, 755–756.
- Ito, T. (1950). *X-ray Studies on Polymorphism*. Tokyo: Maruzen Company.
- Karen, V. L. & Mighell, A. D. (1991). *Converse-transformation analysis*. *J. Appl. Cryst.* **24**, 1076–1078.
- Kariuki, B. M., Belmonte, S. A., McMahon, M. I., Johnston, R. L., Harris, K. D. M. & Nelmes, R. J. (1999). *A new approach for indexing powder*