Journal of
Applied Crystallography
ISSN 0021-8898

book reviews

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Structure determination from powder diffraction data. Edited by W. I. F. David, K. Shankland, L. M. McCusker & Ch. Baerlocher. **International Union of Crystallography Monographs on Crystallography** No. 13. Oxford: IUCr/Oxford University Press, 2002. Pp. xvii + 337. Price GBP 70.00. ISBN 0-19-850091-2.

Ab initio structure solution using powder diffraction data from materials for which no suitable single crystals are available has been one of the most important developments in powder methods during the past twenty years or more. It has contributed significantly to the development of new classes of materials, such as high-temperature superconductors and zeolites, and is currently proving invaluable in characterizing pharmaceutical compounds. However, it is also one of the more demanding applications of powder diffraction; the three-dimensional information available from single-crystal data is collapsed onto the single dimension of a powder diffraction pattern, with a consequent loss of information. The central problem of structure solution is thus the geometric reconstruction of the reciprocal lattice. The long awaited *Structure determination from powder diffraction data*, effectively a sequel to *The Rietveld method*, Monograph No. 5 in this series, describes in detail the various steps necessary to bring this about.

In an admirable introductory chapter, the editors compare the structure determination process with finding the best way through a maze, starting with the sample and ending with the final structure at the centre. There are several paths through the maze and the main purpose of the book is to guide the reader along an optimal route that is appropriate or feasible for a given problem. A. K. Cheetham then provides an overview of the historical background (chapter 2). Powder data have of course been used to determine relatively simple crystal structures since the early days of crystallography, but the methods employed were largely a combination of logical deduction and trial and error. It was mainly the introduction of the Rietveld method for structure refinement and the development of powerful indexing methods that paved the way for what is now known as *ab initio* structure determination from powder data, a technique pioneered by Werner and his colleagues in the late 1970s using data collected with a Guinier–Hägg camera.

As pointed out by the editors, the process is sequential, with each stage depending on the successful completion of the previous steps, and this is more-or-less reflected in the ordering of the chapters. However, for some reason the first stages in the procedure, namely sample preparation, instrument selection and data collection, are deferred until chapter 6, by R. J. Hill and I. C. Madsen. Indeed, this could be regarded as the most important chapter in the book, since its content influences the success or otherwise of the end result of the whole process. Data for various stages in the analysis have different requirements and Hill recommends that at least four and possibly five datasets are obtained, under different experimental conditions and not necessarily using the same sample. How to avoid or minimize systematic errors owing to the sample and the instrument is discussed and optimization of experimental strategy is considered. The latter is particularly important if only limited time is available for data collection. Much of the information in chapter 6 is in fact relevant to other applications of powder diffraction.

The use of various sources of radiation, conventional X-ray tubes, synchrotron radiation and neutrons, is considered in chapters 3, 4 and 5. Their relative merits are discussed in chapter 6, but many crystallographers do not have access to synchrotron X-rays or neutron sources. D. Louër demonstrates in chapter 3 that structure solution can readily be undertaken with data from what are generally known as 'laboratory-based X-ray diffractometers'. Indeed, the majority of moderately complex structures solved by means of powder diffraction have been based on such data. However, high-resolution instruments and good data are needed and Louër describes how these criteria can be met. In chapter 4, P. W. Stevens, D. E. Cox and A. N. Fitch show how the special properties of a synchrotron source can be used to advantage in providing data for structure solution. The high spectral brightness, high degree of collimation and tunability make synchrotron X-rays the ideal source for this purpose. The disadvantages for routine work are limited access and the likelihood of a long lead time for experiments. Neutron powder diffraction data are generally more suited to structure refinement than solution, but R. M. Ibberson and W. I. F. David point out in chapter 5 that this is an over-simplification; there are several instances where it is advantageous to use thermal neutrons, particularly with time-of-flight diffractometers. They also demonstrate that the combination of X-ray and neutron data provides a powerful tool for structure solution. Structures of greater complexity can be solved and the latter helps to locate light atoms.

A crucial step in structure solution is a determination of the unit-cell dimensions from peak positions, leading to a reconstruction of the three-dimensional crystal lattice from the one-dimensional positions of reflections in the powder pattern. This procedure, often known as autoindexing, is covered in chapter 7, by P.-E. Werner. The three principal and most widely used indexing programs are considered and compared, and potential pitfalls are discussed. As Werner points out, all the programs are dependent, in different ways, on having data of high quality, with relatively small systematic errors. It is therefore often desirable to compare the results from different programs. Indexing is one of the success stories of powder diffraction. With accurate peak positions, combined with other available information about the sample, the unit cell and crystal lattice can usually be determined with confidence, provided that any unindexed lines can be attributed to impurities.

The next two chapters deal with the theoretical and experimental aspects of one of the basic problems of structure solution from powder data, namely that of extracting integrated intensities from overlapping reflections. Although the procedure is relatively straightforward, the success of structure solution depends on obtaining as many single-crystal-like intensities as possible. In chapter 9 it is shown that, for some materials, the number can be increased by collecting datasets under different experi-

mental conditions. A by-product of intensity extraction is the determination of one or more possible space groups.

Methods for solving the structure are covered in chapters 10 to 16. These are grouped as adaptations of standard single-crystal techniques, direct-space methods based on prior chemical knowledge, and a combination of the two. In chapter 11 there is a useful list of pitfalls to avoid when using powder data. Although this is specifically aimed at users of direct methods, several of the items listed are applicable generally. Other methods adapted to powder diffraction data are Patterson techniques and the maximum-entropy approach (chapters 13 and 14). Direct-space methods, global optimization strategies (chapter 15) and simulated annealing (chapter 16), were mainly, but not exclusively, developed for molecular compounds. They involve creating a plausible structural model and then assessing its validity by comparing calculated and experimental powder patterns. Extraction of the intensity of individual reflections is thus avoided in this approach.

As mentioned in chapter 1, the final stage in the process is refinement of the structure by means of the Rietveld method; this should confirm the correctness of the solution, but it can also reveal inadequacies in the structural model. The method is not treated separately, though there are references to it throughout the book. It is presumed that the reader will refer the IUCr Monograph on Crystallography No. 5 for details, but an overview of the method would have been desirable, if only for completeness and to emphasize that it is a key stage of the process.

In the final chapter, L. B. McCusker and Ch. Baerlocher stress the importance of using additional information, such as chemical composition, physical properties, structural features of related compounds and the results of non-diffraction experiments. These factors can help to offset the relatively low information content of a powder pattern, compared with a single-crystal dataset. McCusker and Baerlocher show how the extra information can be used at every stage, from data collection onwards. This important chapter should therefore be read at the outset, in conjunction with chapter 6, since its content can influence strategy in subsequent stages.

The book concludes with a list of the principal computer programs needed for structure solution from powder data, but there is no mention here of the Collaborative Computational Project No. 14. Crystallographic software for powder diffraction is freely available from the CCP14 website (http://www.ccp14.ac.uk) for use by students and academia. Most of the listed programs can be downloaded, either directly from the site or *via* appropriate links. Although the site is updated regularly, users should check that they are using the latest version of programs.

This monograph is the eventual outcome of the International Workshop on Structure Determination from Powder Data held at Wadham College, Oxford, in July 1995. The authors all have considerable expertise in the field and many of them contributed to the workshop, but the book is not a Proceedings as such. However, much of it appears to have been drafted some years ago, judging from the references cited, though some authors have included more recent examples. Indeed, a valuable feature is the use of copious examples throughout, to illustrate the key stages of the process, and there are references to other work covering a wide range of materials. The book is an essential and complete text for newcomers to structure solution from powder data and those who are familiar with the technique should find much of interest in its pages.

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books received

The following books have been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally, a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Perovskites modern and ancient. By Roger H. Mitchell. Thunder Bay, Ontario: Almaz Press, 2002. Price USD 70.00. ISBN 0-9689411-0-9

A review of this book, by A. M. Glazer, has been published in the December 2002 issue of *Acta Cryst.* Section B, page 1075.