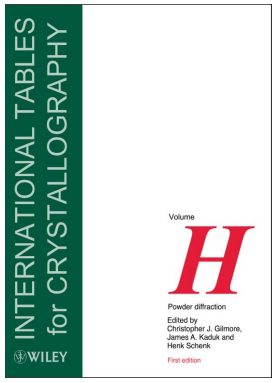
JOURNAL OF APPLIED CRYSTALLOGRAPHY
ISSN 1600-5767

International Tables for Crystallography, Volume H, Powder Diffraction. First edition. Edited by Christopher J. Gilmore, James A. Kaduk and Henk Schenk. Wiley, 2019. Pp. xxxiii + 904. Price (hardcover) GBP 320.00. ISBN 978-1-118-41628-0.

Leopoldo Suescun*

Cryssmat-Lab/DETEMA, Facultad de Química, Universidad de la República, Avenida General Flores 2124, Montevideo 11800, Uruguay. *Correspondence e-mail: leopoldo@fq.edu.uy

Keywords: book reviews; *International Tables for Crystallography*; powder diffraction.



Volume H of *International Tables for Crystallography*, a long-expected update and expansion of Chapters 2.3–2.6 and 3.4–3.6 of Volume C of *International Tables for Crystallography* (2011) (ITC-Vol. C), has been published.

This 904-page-long book provides a comprehensive description of the powder diffraction method, aimed at novice users who need to familiarize themselves with the details of the method and related techniques based on polycrystals or multiple-particle systems. Furthermore, it provides a very good compilation of fundamentals, methods and case studies useful for the specialist looking for theoretical details, application notes and up-to-date references. This book will soon become an irreplaceable tool for teachers, researchers and students.

The book is divided into seven parts organized as follows: fundamentals (Part 1); instrumentation requirements, both standard and state of the art, and sample preparation tips and tricks (Part 2); methodologies, ranging from instrument alignment and data collection to the many possible aspects of data analysis (Part 3); applications to structure (Part 4) and microstructure (Part 5) determination and analysis; available software (Part 6); and applications and perspectives of powder diffraction for characterizing different families/classes of materials (Part 7). Although the book is mostly devoted to X-rays, neutron and electron powder diffraction are introduced and discussed in Chapters 2.3 and 2.4, respectively. These techniques are also discussed in many examples throughout the text.

A detailed description of each part, with some highlighted chapters, is given below.

Part 1, the *Introduction*, gives the reader an overview of the concepts required to understand the information contained in a powder diffraction pattern (diffractogram). It follows a logical approach, starting with peak positions, then moving to peak intensities and peak shapes, and finally background, in Sections 1.1.1–1.1.5, respectively. Bragg's law is first introduced, then reciprocal space and Laue equations are covered, and finally the Ewald sphere and Debye rings are described. The nomenclature used for the scattering vector (**h**) and related direct- and reciprocal-space magnitudes is consistent with that used in the *Online Dictionary of Crystallography* (https://dictionary.iucr.org/Main_Page), which is much appreciated. Peak intensities are discussed very briefly. The structure factor is calculated from the sum of all scattered waves from individual atoms in a crystal [the reader is directed to the discussion of atomic scattering factors (f_j) in ITC-Vol. C], later using the periodicity to restrict the sum to one unit cell. Finally, the scattered intensity from a powder, including all required corrections, is presented. Profile shapes are described using convolution and Fourier transform equations that will later be derived in detail, such as Scherrer's formula and microstrain broadening (Chapters 5.1 and 5.2). A long digression leading to atomic pair distribution function analysis is given when the background is discussed (Section 1.1.5). This finally leads, in Section 1.1.6, to a first mention of Rietveld analysis combined with structure determination, local structure and parametric refinements. The end of the *Introduction* is a one-paragraph *Outlook* section (1.1.7) with a concise discussion on why powder diffraction has been and will continue to be so relevant to the materials community, despite progress in electron

diffraction and synchrotron single-crystal instrumentation that has enabled structure solution with samples of the size of one powder grain.

Part 2 is devoted to *Instrumentation and sample preparation* and is the longest (197 pages), thus stressing the experimental nature of this area of crystallography. Experts on experimental techniques and instrumentation take the reader from conventional in-house powder diffractometry to the latest developments in *in situ* multi-technique characterization of polycrystalline materials. Sample preparation advice for each type of experiment is given. Chapter 2.1 explores all aspects of in-house laboratory equipment, focusing on relevant details of the widely used Bragg–Brentano geometry. Frequent alignment errors and corrections are discussed, and geometries for non-routine powder/polycrystalline diffractometry are described. Non-expert users who wish to learn about different options for in-house instrumentation will find this chapter enlightening. Chapter 2.2 focuses on powder diffraction using synchrotron radiation; production of X-rays, monochromatization, instrumentation and details of choice of instrument parameters for specific applications are discussed. This chapter highlights the main advantages of synchrotron radiation relative to in-house instruments, including anomalous/resonant scattering and specialized fast data collection instruments for *in situ*/*operando* experiments. Chapter 2.3 focuses on neutron powder diffraction. Most of its initial section emphasizes the complementarity of this technique with X-ray diffraction. A detailed section on neutron production follows, covering both reactor and spallation sources. A neutron powder diffraction instrumentation section completes an up-to-date review of the state-of-the-art neutron powder diffraction multi-user facilities. A succinct review of the type of experiments that could be performed to characterize powder and polycrystalline samples concludes the chapter. Although magnetic neutron diffraction is mentioned, no details are given; as a result, Part 6 of ITC-Vol. C remains the only source of magnetic neutron diffraction in the *International Tables* series. Chapter 2.4 gives a brief description of electron powder diffraction. This chapter is too short to provide the reader with an adequate perspective of the technique; references to figures and tables from other books are overabundant. The most interesting parts of the chapter are those devoted to texture, Rietveld and future applications of the pair-distribution-function analysis of electron diffraction data. Chapter 2.5 deals with two-dimensional powder diffractometry and provides extensive geometrical details, as well as a derivation of scattering equations for the purpose of describing each pixel of an area detector used in powder diffraction. It is a very good introduction to the experimental details of texture and microstructure analysis and to the newest trends of powder diffractometers for non-conventional experiments. Chapters 2.6 and 2.7 are devoted to non-ambient-temperature and high-pressure powder diffraction, respectively. They are short and well written with enough examples to give the newcomer a good overview of the requirements, difficulties and possibilities of these methods. Chapter 2.8 discusses powder diffraction in external electric and magnetic fields. Although this chapter overlaps significantly with previous ones, the many interesting examples make up for the repetition. Chapter 2.9 describes cells for *in situ* powder diffraction investigation of chemical reactions. A plethora of reaction chambers and setups for X-ray and neutron powder diffraction are illustrated with results obtained using these setups, making this chapter to the point and practical. The final chapter (2.10) covers powder specimen preparation, both for in-house and for user-facility experiments, and focuses on describing deviations from an ideal powder that result from poor sample preparation and how to avoid such issues. It is also an excellent reminder that no data set is better than the sample used to collect it. Again, a plethora of examples are provided; special sample holders to facilitate proper sample preparation are described, and practical advice is given. This chapter is indispensable for any user of powder diffraction instruments, whether in house or user-facility based.

Part 3 focuses on *Methodology*, giving an in-depth treatment of some of the concepts set out in the *Introduction*. Chapter 3.1 describes all the elements of a conventional diffractometer and the step-by-step alignment process to obtain the best possible powder diffraction pattern. It will be very useful for scientists and technicians who need to take care of an in-house instrument on a daily basis. Chapter 3.2 deals with diffraction physics. All relevant equations to understand the observed powder diffraction intensities are presented. It is the only chapter where some phenomena relevant to quantitative phase analysis such as microabsorption, surface roughness and extinction are discussed. Texture and anisotropic strain broadening are also covered, with a focus on modelling profile widths. Anisotropic strain broadening is again treated in Chapter 3.3, which is devoted to modelling powder diffraction peak profiles for different experimental techniques. These two chapters are particularly relevant for users of the Rietveld method because profile modelling is a common issue for beginners. Chapter 3.4 deals with indexing of powder diffraction patterns from unknown phases. The challenge behind indexing a pattern is described, as well as how the success of the indexing process is assessed; details of the computations performed by the different indexing methods are wisely skipped. The most successful traditional indexing programs and some new approaches developed in the past three decades are discussed, including examples of use of free and commercial programs. Chapter 3.5 deals with intensity extraction and data reduction, *i.e.* how to obtain the observed structure factor modulus from an indexed powder diffractogram. The material presented in this chapter relies heavily on assumptions made in the Rietveld method, which has not been treated extensively at this point. Chapter 3.6 discusses whole powder pattern modelling, aiming to determine particle size, strain defects and other microstructural features of the sample without the use of structure factors. It is a long chapter with a significant number of complex equations that are very well contextualized and illustrated by examples, making this chapter instructive for beginners. Crystallographic databases are discussed in Chapter 3.7, with a very strong focus on the

Powder Diffraction File (PDF) from the International Centre for Diffraction Data. This database is the product of extensive international collaboration for the compilation of accurate powder diffraction data from different sources and in different formats with physical and chemical context. Currently, this database provides both calculated and experimental powder diffraction patterns, which makes it a comprehensive tool for users. This chapter also covers other relevant crystallographic databases that contain structural details, such as the Cambridge Structural Database, the Inorganic Crystal Structure Database, the Protein Data Bank, Pearson's Crystal Data and the Crystallography Open Database. More specific databases devoted to metals, minerals and zeolites are mentioned too. Also discussed in this chapter is the search–match process of identifying phases in a powder diffractogram. This discussion contains a very interesting series of examples using the PDF-2 database. Chapter 3.8 focuses on clustering and visualization of powder diffraction data, with application to sequential or multi-sample studies. This is a new and exciting area of powder diffraction analysis, brought about by the availabilty of robotic instruments and *in situ* studies at user facilities; as such, it deserved to be included in this part. Correlation coefficients that are used to identify similarities and differences between diffraction patterns (or spectra in general) are described, finally leading to the identification of groups of powder patterns by similarity in composition (cluster analysis). The chapter layout, however, is far from satisfying. The examples presented throughout the chapter are worth reading, including a multi-technique analysis combining powder diffraction and Raman spectroscopy data. This chapter requires significant improvements in future editions. Finally, Chapters 3.9 and 3.10 describe quantitative phase analysis methods based on individual peak intensities and the Rietveld method, respectively. The accuracy of the results obtained with the latter with regards to quantification of phases is also discussed. These two are very well written chapters that present the fundamentals in a didactic manner and discuss several examples from different disciplines, including data that the reader can download and analyse on his/her own.

Part 4 is entirely devoted to structure determination using powder diffraction data. The opening chapter (4.1) begins with a presentation of the problem underpinning structure determination using powder diffraction data and an overview of relevant methods to tackle this challenge. Chapters 4.2 and 4.3 discuss the structure determination of molecular crystal structures by reciprocal-space and direct-space methods, respectively. Both chapters are very didactic; they skip the deep mathematical details yet discuss many methods and programs and use multiple examples to illustrate how structures may be successfully determined. Chapter 4.4 shows how to incorporate supplementary crystallographic information into a structure solution procedure, with examples and test data. Chapter 4.5 is devoted to structure determination and refinement of inorganic structures, where the inclusion of restraints for polyhedral coordination and connectivity is important. Chapter 4.6 introduces the reader to the world of zeolites and their structure determination and refinement. Similarly to other chapters, it provides a good introduction for the beginner and is full of examples. Chapter 4.7 is devoted to the history and working principles underlying Rietveld refinement. This chapter is entirely descriptive, with no figures or examples given, yet very useful for understanding how and why the method works and the details of its implementation in computer programs. Chapter 4.8 introduces and discusses the maximum-entropy method (MEM) for refining structures from powder diffraction data. A number of detailed examples help the reader follow the strategy of refinement programs and MEM-assisted structure determination with the charge-flipping method. Chapter 4.9 discusses the required steps for validation of a structure determined from powder diffraction data. This is a very useful chapter that helps the reader identify key points to assess the quality of the refined structural model and what could reasonably be obtained from a structural Rietveld refinement based on a specific data set. This discussion is mostly based on examples from different types of materials. Part 4 closes with Chapter 4.10, which introduces and discusses reporting of structures, data and fit results using the powder-diffraction-oriented Crystallographic Information File standard (pdCIF) in the broader context of the general CIF. The last two chapters are a must-read for students and researchers who aim to publish in this area.

Part 5 provides an in-depth description of the impact of defects, texture and microstructure on a powder diffraction pattern, expanding on concepts first introduced in Section 1.1.4. None of the relevant equations are skipped and a detailed derivation of each one of them is given. Chapter 5.1 explains the origin of size broadening and derives Scherrer's formula, emphasizing the limited applicability of its most simplified version. Chapter 5.2 deals with stress and strain. The chapter contains no figures or examples, making it one of the less didactic of the book. Chapter 5.3 discusses quantitative texture analysis, including the study of samples with texture, defects and microstructural effects. The chapter contains many examples, making it very approachable for the beginner as well as useful for the expert looking for more details. Chapter 5.4 introduces thin-film and multilayer analysis by diffraction techniques, including diffraction and reflectivity characterization; this is an important addition to the *International Tables for Crystallography* series. The chapter discusses instrumental requirements and different configurations, and also provides an engaging perspectives section that highlights future challenges in this area. Chapter 5.5 discusses multigrain crystallography and three-dimensional grain mapping. These are also new techniques that were born from modern synchrotron sources with micro/nanometre-focused and coherent beams. The chapter provides examples and experimental details that help the reader understand the basics and results that may be obtained. Chapter 5.6 is devoted to X-ray diffraction from non-crystalline materials and the Debye model. This is an enlightening chapter showing how much information is available in peakless patterns and in the background of partially crystalline samples. It is the perfect transition to Chapter 5.7, which is devoted to total scattering

and atomic pair distribution function (PDF) analysis; special emphasis is placed on the nanostructure problem. This is also a very didactic chapter, without skipping the mathematical formulation, and includes plenty of easy-to-follow examples and details. It discusses X-ray, neutron and even electron PDF analysis, including data reduction and processing, structural analysis, and determination using total scattering data. Chapter 5.8 goes one step beyond Chapter 5.7 and discusses the characterization of disordered heterogeneous materials by small-angle scattering techniques. In this chapter, the nanostructure problem is discussed beyond the atomic structure of the nanoparticle, with a focus on the nano- to submicrometric scale. Small-angle X-ray and neutron scattering are presented, including magnetic small-angle neutron scattering, with a good number of applications and examples and a very inspiring perspectives subsection.

Part 6 contains a table with a survey of ∼200 computer programs and software packages for powder diffraction data analysis in all of the areas discussed in the book. Although it is not expected that such a complete list of programs will remain accurate for a long time, it is surprising that more than 15% of the programs listed could not be found at the given web addresses, maybe due to the COVID-19 pandemic; furthermore, five of them appear to be permanently unavailable.[1]

Part 7 contains 14 different chapters, unrelated to each other, where applications of powder diffraction are shown. The relevance of the Rietveld method to the analysis of powder diffraction data is highlighted in this part, with 12 of the 14 chapters discussing at least one example of its use. This is the perfect place to find examples for a dissemination lecture or an introductory powder diffraction course. The applications that are discussed are macromolecular crystallography (7.1), forensic science (7.2), materials for energy storage and conversion (mainly Li-ion batteries) (7.3), arts and archaeology (7.4), pharmaceuticals (7.5), and mining and minerals processing (7.7), along with specific chapters on aluminium ores (7.6), the petroleum and petrochemical industries (7.11), and cements (7.12). Ceramic and glass-ceramic materials are discussed in sections 7.8 and 7.9, respectively, followed by industrial organic pigments (7.10), superconductors (7.13) and finally minerals (7.14). Each reader will find at least one chapter on his/her area of interest, regardless of the area of powder diffraction (or crystallography in general) they come from. Noteworthy is the final chapter of the book, entitled *Powder diffraction by minerals*, which instead of focusing on past achievements highlights the challenges and future developments needed to address the most important questions in the area today; this makes it one of the most inspiring chapters of the book.

As in every first edition of this kind of multi-author book, a number of nomenclature discrepancies and repetitions are found that may be corrected or better addressed in future editions.[1] Use of colour is very uneven through the book: many figures, but especially those in Chapter 4.5, would immensely benefit from it. In many chapters, examples of results obtained with different programs are given, extracted from the literature or from the author's database. Having more of these data sets available for the reader to reproduce the results given would be a great addition to the book. Finally, an index of phases for which powder patterns are shown would also be a good addition to a second edition of the book, since a search for phases would quickly help the reader identify interesting characteristics or frequent problems of his/her samples and relevant literature.

In summary, *International Tables for Crystallography* Volume H is a book that the community has been long expecting from the IUCr. It will undoubtedly occupy an important place on the shelves or desks of every modern powder diffraction laboratory, especially multi-user laboratories where researchers with different backgrounds could benefit from the fundamentals, multiplicity of practical advice, examples, and up-to-date bibliography presented in each chapter of the book. This book should be celebrated as an achievement of the Editors, the authors, and the well established and broad community of powder diffraction users.

Acknowledgements

The author thanks Professor F. Rabuffetti for his revision and English language editing of this review.

References

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[1] A list of corrections, including updated addresses for computer programs that have changed sites, has been communicated to the Editors of Volume H, and corrections to be included in the next edition will be posted on the *International Tables* web site (https://it.iucr.org/H/) in due course.