Preface

A little over five years have passed since the first edition of this book appeared in print. Seems like an instant but also eternity, especially considering numerous developments in the hardware and software that have made it from the laboratory test beds into the real world of powder diffraction. This prompted a revision, which had to be beyond cosmetic limits. The book was, and remains focused on standard laboratory powder diffractometry. It is still meant to be used as a text for teaching students about the capabilities and limitations of the powder diffraction method. We also hope that it goes beyond a simple text, and therefore, is useful as a reference to practitioners of the technique.

The original book had seven long chapters that may have made its use as a text inconvenient. So the second edition is broken down into 25 shorter chapters. The first fifteen are concerned with the fundamentals of powder diffraction, which makes it much more logical, considering a typical 16-week long semester. The last ten chapters are concerned with practical examples of structure solution and refinement, which were preserved from the first edition and expanded by another example – solving the crystal structure of Tylenol®.

Major revisions include an expanded discussion of nonconventional crystallographic symmetry in Chap. 5, a short description of two new types of detectors that are becoming common in laboratory powder diffractometry – real-time multiple strip and multi wire detectors in Chap. 6, a brief introduction to the total scattering analysis in Chap. 10, a short section in Chap. 11 describing nonambient powder diffractometry, an expanded discussion of quantitative phase analysis, including the basics of how to quantify amorphous component in Chap. 13, an update about the recent advancements in the ab initio indexing, together with an example of a difficult pseudo-symmetric case represented by $Li[B(C_2O_4)_2]$, and a major update of Chap. 15 dedicated to the fundamentals of Rietveld analysis, including a brief introduction of the mechanism of restraints, constraints, and rigid bodies. The collection of problems that may be used by instructors to assess students' progress and as self-exercises has also expanded. All problems related to the solution and refinement of crystal structures from powder diffraction data are assembled at the end of Chap. 25.

Considering all these additions, something had to go. A major deletion from the earlier paper version is the section on X-ray safety, which has been moved to the electronic part of the book. Readers familiar with the first edition know that the book included a CD with electronic figures, experimental data, and solutions of all problems. Over the years, both the publisher and we have had numerous inquiries from people who accidentally used the CD as a coaster, clay pigeon, or simply sat on it before making a backup copy. While each and every request about sending a copy of the CD was fulfilled, we thought that it makes more sense to have the electronic files available online. The files are hosted by Springer (http://www.springer.com/978-0-387-09578-3) and they are made available to everyone who has the book. The files include color figures, powder diffraction data, examples, web links, and solutions to all the problems found throughout the book. Files with the solutions of the problems are only available to instructors, who must register with the publisher.

Finally, we would like to thank everyone who provided critique and feedback. Most important, we thank the readers who opted to buy our book with their hard-earned money thus providing enough votes for the publisher to consider this second, revised edition. It is our hope that this edition is met with even better acceptance by our readers of students, practitioners, and instructors of the truly basic materials characterization technique, which is the powder diffraction method.

Ames, Iowa, October 2008 *Vitalij K. Pecharsky*
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Preface to the First Edition

Without a doubt, crystals such as diamonds, emeralds and rubies, whose beauty has been exposed by jewelry-makers for centuries, are enjoyed by everybody for their perfect shapes and astonishing range of colors. Far fewer people take pleasure in the internal harmony – atomic structure – which defines shapes and other properties of crystals but remains invisible to the naked eye. Ordered atomic structures are present in a variety of common materials, for example, metals, sand, rocks or ice, in addition to the easily recognizable precious stones. The former usually consist of many tiny crystals and therefore, are called polycrystals, for example metals and ice, or powders, such as sand and snow. Besides external shapes and internal structures, the beauty of crystals can be appreciated from an infinite number of distinct diffraction patterns they form upon interaction with certain types of waves, for example, X-rays. Similarly, the beauty of the sea is largely defined by a continuously changing but distinctive patterns formed by waves on the water's surface.

Diffraction patterns from powders are recorded as numerical functions of a single independent variable, the Bragg angle, and they are striking in their fundamental simplicity. Yet, a well-executed experiment encompasses an extraordinarily rich variety of structural information, which is encoded in a material- and instrument-specific distribution of the intensity of coherently scattered monochromatic waves whose wavelengths are commensurate with lattice spacing. The utility of the powder diffraction method – one of the most essential tools in the structural characterization of materials – has been tested for over 90 years of successful use in both academia and industry. A broad range of general-purpose and specialized powder diffractometers are commonly available today, and just about every research project that involves polycrystalline solids inevitably begins with collecting a powder diffraction pattern. The pattern is then examined to establish or verify phase composition, purity, and the structure of the newly prepared material. In fact, at least a basic identification by employing powder diffraction data as a fingerprint of a substance, coupled with search-and-match among hundreds of thousands of known powder diffraction patterns stored in various databases, is an unwritten mandate for every serious work that involves crystalline matter.

Throughout the long history of the technique, its emphasis underwent several evolutionary and revolutionary transformations. Remarkably, the new developments have neither taken away, nor diminished the value of earlier applications of the powder diffraction method; on the contrary, they enhanced and made them more precise and dependable. A noteworthy example is phase identification from powder-diffraction data, which dates back to the late 1930s (Hanawalt, Rinn, and Frevel). Over the years, this application evolved into the Powder Diffraction File™ containing reliable patterns of some 300,000 crystalline materials in a readily searchable database format (Powder Diffraction File is maintained and distributed by the International Centre for Diffraction Data, http://www.icdd.com).

As it often happens in science and engineering, certain innovations may go unnoticed for some time but when a critical mass is reached or exceeded, they stimulate unprecedented growth and expansion, never thought possible in the past. Both the significance and applications of the powder diffraction method have been drastically affected by several directly related as well as seemingly unrelated developments that have occurred in the recent past. First was the widespread transition from analogue (X-ray film) to digital (point, line, and area detectors) recording of scattered intensity, which resulted in the improved precision and resolution of the data. Second was the groundbreaking work by Rietveld, Young and many others, who showed that full profile powder diffraction data may be directly employed in structure refinement and solution. Third was the availability of personal computers, which not only function as instrument controllers, but also provide the much needed and readily available computing power. Computers thus enable the processing of large arrays of data collected in an average powder diffraction experiment. Fourth was the invention and rapid evolution of the internet, which puts a variety of excellent, thoroughly tested computer codes at everyone's fingertips, thanks to the visionary efforts of many bright and dedicated crystallographers.

Collectively, these major developments resulted in the revolutionary changes and opened new horizons for the powder diffraction technique. Not so long ago, if you wanted to establish the crystal structure of a material at the atomic resolution, virtually the only reliable choice was to grow an appropriate quality single crystal. Only then could one proceed with the collection of diffraction data from the crystal followed by a suitable data processing to solve the structure and refine relevant structural parameters. A common misconception among the majority of crystallographers was that powder diffraction has a well-defined niche, which is limited to phase identification and precise determination of unit cell dimensions. Over the past ten to twenty years the playing field has changed dramatically, and the ab initio structure determination from powder diffraction data is now a reality. This raises the bar and offers no excuse for those who sidestep the opportunity to establish details of the distribution of atoms in the crystal lattice of every polycrystalline material, whose properties are under examination. Indeed, accurate structural knowledge obtained from polycrystals is now within reach. We believe that it will eventually lead to a much better understanding of structure-property relationships, which are critical for future advancements in materials science, chemistry, physics, natural sciences, and engineering.

Before a brief summary recounting the subject of this book, we are obliged to mention that our work was not conducted in a vacuum. Excellent texts describing the powder diffraction method have been written, published, and used by the generations of professors teaching the subject and by the generations of students learning the trade in the past. Traditional applications of the technique have been exceptionally well-covered by Klug and Alexander (1954), Azaroff and Buerger (1958), Lipson and Steeple (1970), Cullity (1956 and 1978), Jenkins and Snyder (1996), and Cullity and Stock (2001). There has never been a lack of reports describing the modern capabilities of powder diffraction, and they remain abundant in technical literature (Journal of Applied Crystallography, Acta Crystallographica, Powder Diffraction, Rigaku Journal, and others). A collective monograph, dedicated entirely to the Rietveld method, was edited by Young and published in 1993. A second collection of reviews, describing the state of the art in structure determination from powder diffraction data, appeared in 2002, and it was edited by David, Shankland, McCusker, and Baerlocher. These two outstanding and highly professional monographs are a part of the multiple-volume series sponsored by the International Union of Crystallography, and are solid indicators that the powder diffraction method has been indeed transformed into a powerful and precise, yet readily accessible, structure determination tool. We highly recommend all the books mentioned in this paragraph as additional reading to everyone, although the older editions are out of print.

Our primary motivation for this work was the absence of a suitable text that can be used by both the undergraduate and graduate students interested in pursuing in-depth knowledge and gaining practical experience in the application of the powder diffraction method to structure solution and refinement. Here, we place emphasis on powder diffraction data collected using conventional X-ray sources and general-purpose powder diffractometers, which remain primary tools for thousands of researchers and students in their daily experimental work. Brilliant synchrotron and powerful neutron sources, which are currently operational or in the process of becoming so around the world, are only briefly mentioned. Both may, and often do provide unique experimental data, which are out-of-reach for conventional powder diffraction especially when high pressure, high and low temperature, and other extreme environments are of concern. The truth, however, is that the beam time is precious, and both synchrotron and neutron sources are unlikely to become available to everyone on a daily basis. Moreover, diffraction fundamentals remain the same, regardless of the nature of the employed radiation and the brilliance of the source.

This book has spawned from our affection and lasting involvement with the technique, which began long ago in a different country, when both of us were working our way through the undergraduate and then graduate programs in Inorganic Chemistry at L'viv State University, one of the oldest and finest institutions of higher education in Ukraine. As we moved along, powder diffraction has always remained on top of our research and teaching engagements. The major emphasis of our research is to obtain a better understanding of the structure–property relationships of crystalline materials, and both of us teach graduate-level powder diffraction courses at our respective departments – Materials Science and Engineering at Iowa State University and Chemistry at the State University of New York (SUNY) at Binghamton.

Even before we started talking about this book, we were unanimous in our goals: the syllabi of two different courses were independently designed to be useful for any background, including materials science, solid-state chemistry, physics, mineralogy, and literally any other area of science and engineering, where structural information at the atomic resolution is in demand. This philosophy, we hope, resulted in a text that requires no prior knowledge of the subject. Readers are expected to have a general scientific and mathematical background of the order of the first two years of a typical liberal arts and sciences or engineering college.

The book is divided into seven chapters. The first chapter deals with essential concepts of crystallographic symmetry, which are intended to facilitate both the understanding and appreciation of crystal structures. This chapter will also prepare the reader for the realization of the capabilities and limitations of the powder diffraction method. It begins with the well-established notions of the three-dimensional periodicity of crystal lattices and conventional crystallographic symmetry. It ends with a brief introduction to the relatively young subject – the symmetry of aperiodic crystals. Properties and interactions of symmetry elements, including examination of both point and space groups, the concept of reciprocal space, which is employed to represent diffraction from crystalline solids, and the formal algebraic treatment of crystallographic symmetry are introduced and discussed to the extent needed in the context of the book.

The second chapter is dedicated to properties and sources of radiation suitable for powder diffraction analysis, and gives an overview of the kinematical theory of diffraction along with its consequences in structure determination. Here, readers learn that the diffraction pattern of a crystal is a transformation of an ordered atomic structure into a reciprocal space rather than a direct image of the former. Diffraction from crystalline matter, specifically from polycrystalline materials is described as a function of crystal symmetry, atomic structure, and conditions of the experiment. The chapter ends with a general introduction to numerical techniques enabling the restoration of the three-dimensional distribution of atoms in a lattice by the transformation of the diffraction pattern back into direct space.

The third chapter begins with a brief historical overview describing the powder diffraction method and explains the principles, similarities, and differences among the variety of powder diffractometers available today. Since ionizing radiation and highly penetrating and energetic particles are employed in powder diffraction, safety is always a primary concern. Basic safety issues are concisely spelled out using policies and procedures established at the US DOE's Ames Laboratory as a practical example. Sample preparation and proper selection of experimental conditions are exceedingly important in the successful implementation of the technique. Therefore, the remainder of this chapter is dedicated to a variety of issues associated with specimen preparation, data collection, and analysis of most common systematic errors that have an impact on every powder diffraction experiment.

Beginning from chapter four, key issues that arise during the interpretation of powder diffraction data, eventually leading to structure determination, are considered in detail and illustrated by a variety of practical examples. This chapter describes preliminary processing of experimental data, which is critical in both qualitative and quantitative phase analyses. In addition to a brief overview of phase identification techniques and quantitative analysis, readers will learn how to determine both the integrated intensities and angles of the observed Bragg peaks with the highest achievable precision.

Chapter five deals with the first major hurdle, which is encountered in powder diffraction analysis: unavoidably, the determination of any crystal structure starts from finding the shape, symmetry, and dimensions of the unit cell of the crystal lattice. In powder diffraction, finding the true unit cell from first principles may present considerable difficulty because experimental data are a one-dimensional projection of the three-dimensional reciprocal lattice. This chapter, therefore, introduces the reader to a variety of numerical techniques that result in the determination of precise unit cell dimensions. The theoretical background is followed by multiple practical examples with varying complexity.

Chapter six is dedicated to the solution of materials' structures, that is, here we learn how to find the distribution of atoms in the unit cell and create a complete or partial model of the crystal structure. The problem is generally far from trivial, and many structure solution cases in powder diffraction remain unique. Although structure determination from powder data is not a wide-open and straight highway, knowing where to enter, how to proceed, and where and when to exit is equally vital. Hence, in this chapter both direct and reciprocal space approaches and some practical applications of the theory of kinematical diffraction to solving crystal structures from powder data are explained and broadly illustrated. Practical examples start from simple, nearly transparent cases, and end with quite complex inorganic structures.

The solution of a crystal structure is considered complete only when multiple profile variables and crystallographic parameters of a model have been fully refined against the observed powder diffraction data. Thus, the last, the seventh chapter of this book describes the refinement technique, most commonly employed today, which is based on the idea suggested in the middle 1960s by Rietveld. Successful practical use of the Rietveld method, though directly related to the quality of powder diffraction data (the higher the quality, the more reliable the outcome), largely depends on the experience and the ability of the user to properly select a sequence in which various groups of parameters are refined. In this chapter, we introduce the basic theory of Rietveld's approach, followed by a series of hands-on examples that demonstrate the refinement of crystal structures with various degrees of completeness and complexity, models of which were partially or completely built in chapter six.

The book is supplemented by an electronic volume – compact disk – containing powder diffraction data collected from a variety of materials that are used as examples and in the problems offered at the end of every chapter. In addition, electronic versions of some 330 illustrations found throughout the book are also on the CD. Electronic illustrations, which we hope is useful to both instructors and students because electronic figures are in color, are located in a separate folder /Figures on the CD. Three additional folders named /Problems, /Examples and /Solutions contain experimental data, which are required for solving problems, as self-exercises, and our solutions to the problems, respectively. The disk is organized as a web page, which makes it easy to navigate. All web links found in the book, are included on the CD and can be followed by simply clicking on them. Every link is current as of January 2003. The compact disk is accessible using both Mac's and PC's, and potential incompatibility problems have been avoided by using portable document, HTML, and ASCII formats.

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