Preface

A detailed insight into atomic-level structure is of crucial importance in understanding, designing and optimizing structural and functional materials. The technique of choice for structure determination is usually single crystal diffraction. Unfortunately, single crystals of suitable size and shape are simply not available for many materials, and one has to rely on powder diffraction methods. These are often viewed as information poor, but actually contain a wealth of information which is not available in a routine single crystal study. Some of this is summarized schematically in Figure 1: Bragg peak intensities give detailed information about a sample’s phase make-up and the composition and structure of phases; peak shapes give information about its microstructure; and the diffuse intensity between the Bragg peaks gives information on various aspects of local structure or disorder. The technique can also be more easily adapted to perform in situ or operando studies than single crystal methods, allowing us to follow materials in action. The information content of a powder pattern is huge, but sophisticated analysis methods are often needed to harvest the maximum amount of information from the data (Dinnebier & Billinge, 2008). This book discusses how this can be done.

Although the powder diffraction method was developed as early as 1916 by Peter Debye and Paul Scherrer (1916), for the first 50 years its use in crystallography was almost exclusively limited to qualitative and semiquantitative phase analysis. In materials science residual stress, texture and microstructure were also heavily investigated. What held the field back, especially in the area of determination of the atomic crystal structure, was the often-cited problem of powder diffraction: the accidental and systematic peak overlap caused by a projection of three-dimensional reciprocal space on to the one-dimensional $2\theta$ axis of a powder pattern. This leads to a strongly reduced information content compared to a single crystal data set. The introduction of what has become known as the Rietveld method marked a turning point (Rietveld, 1967, 1969). Hugo Rietveld created a program to sidestep the overlap problem by modeling the whole powder pattern with a set of parameters that can be refined by minimizing the difference between the calculated and the measured powder pattern. One then finds that there is sufficient information in the one-dimensional data set to reconstruct the three-dimensional structure. The early development of different methods and Rietveld codes has been discussed by various authors (Young 1993, van Laar 2018). A great feature of the Rietveld method is the possibility to separate the main constituents of a powder pattern (background, lattice, crystal structure and microstructure – see Figure 1), allowing different aspects of a material’s properties to be probed separately. We cover the fundamentals of powder diffraction in Chapter 1 and describe the Rietveld whole pattern fitting method in Chapter 2.

In its original implementation, the Rietveld method was used to refine a structural model from neutron diffraction data of single-phase samples. The method has been significantly extended over the last 50 years, and a variety of different whole-pattern fitting techniques are now used. One set is the LeBail (1988) and Pawley (1981) methods...
that are structure-independent whole powder pattern fitting approaches for deriving reflection intensities for structure determination, testing lattice parameters and space groups and for deriving microstructural parameters without the need for a crystal structure. The uses of these and related methods are discussed in Chapter 3.

In the earliest Rietveld codes, the shapes of peaks in a powder pattern were fitted with analytical functions such as Gaussian, Lorentzian or pseudo-Voigt functions, and the $2\theta$-dependence of peak widths was described using simple empirical functions. With increasing computational power it has become possible to develop more sophisticated approaches in which the contributions to the peak shape from the instrument and sample are treated separately giving access to exquisite detail about the microstructure of a material (size, strain and so on). We explore various approaches for this in Chapter 4. Recently, faster and more sophisticated algorithms and much faster computers have allowed Rietveld refinement using large supercells. This allows the description of complex stacking faults as structural contributions to peak shapes during Rietveld refinement (Coelho et al., 2016), and is discussed in Chapter 10.

The extension of the Rietveld method to X-ray powder diffraction data was published in 1977 (Malmros & Thomas, 1977) and has had enormous impact in many different areas. Most obviously, it allows the structural analysis of samples using laboratory-derived data. It has also opened up the possibility of routine quantitative analysis of multiphase mixtures (including amorphous content) by the Rietveld method. This is now a major application of the Rietveld method in industry (Bish

---

**Figure 1:** Schematic view of the different parts of a powder pattern and their physical meaning (adapted from Dinnebier & Billinge (2008) with permission from The Royal Society of Chemistry).
Howard, 1988). We discuss the quantitative phase analysis of crystalline and amorphous samples in Chapter 5.

Chapter 6 introduces some of the ideas that are needed to refine particularly complex structures, where the information content in the powder diffraction data alone may not be sufficient. In these cases, extra information (“chemical knowledge”) can be included in the form of constraints, restraints and rigid bodies. These can help stabilize refinements, and even small protein structures can now be refined using synchrotron powder diffraction data (Von Dreele, 1999). Similar information is also needed if one tries to solve structures ab initio using the Rietveld method coupled with simulated annealing (Newsam et al., 1992). We discuss some of the tricks needed to do this in Chapter 7, but refer the reader to more specialized texts (David et al., 2006) for discussion of other structure solution methods.

Chapter 8 discusses another approach that can help reduce the number of parameters needed in Rietveld refinement of samples that undergo symmetry-lowering phase transitions – so-called symmetry-adapted distortion mode refinements. The method can allow efficient analysis of otherwise complex problems and can help rapidly identify the key structural changes occurring at the transition. The symmetry ideas underlying this approach can be reapplied to a number of related problems such as understanding spin arrangements in magnetically ordered materials, which are covered in Chapter 9. We discuss here how the interaction of neutrons with magnetic moments allows the determination of magnetic structure and some of the different approaches to magnetic Rietveld refinement.

Turning to the bottom left corner of Figure 1, elastic diffuse scattering is measured during any powder diffraction experiment, but is usually ignored during Rietveld refinement and treated as part of the general “background” of the pattern. It is, however, possible to extract information about the local structure of a material from this scattering. With modern X-ray and neutron sources, the powder pattern can be measured over a large range of reciprocal space with good counting statistics. One can then take the Fourier transform of the normalized pattern to produce the real space pair distribution function (PDF) in the so-called total scattering approach. In Chapter 11, we introduce the real-space Rietveld-type approaches to analyzing such data and modeling local structure.

Finally, with modern instrumentation it is now possible to collect a vast number of powder diffraction patterns of a sample as a function of external variables with a time resolution in the second or even sub-second regime. This allows the detailed in situ or operando study of many important processes. In Chapter 12, we describe some of the ways to simulate multiple powder patterns to help plan such experiments. We also discuss how to automate data analysis to allow fitting of large numbers of patterns using either a sequential approach, where each data set is analyzed independently, or a parametric approach, where parameters are refined across multiple data sets (Stinton & Evans, 2007). There are many as yet unexplored applications of these methods.
Over 25 years have passed since the last textbook exclusively devoted to Rietveld refinement (Young, 1993) was published, and there have been significant developments since that time. We therefore decided to write a text that combines the fundamentals of the method with practical details of its implementation. Several powerful public domain Rietveld codes have been developed such as GSAS (Larson & Von Dreele, 1986), FULLPROF (Rodriguez-Carvajal, 1993), RietAN (Izumi, 1989) and JANA (Petricek et al., 2014), to name just a few. When preparing this book, we decided to focus on the academic version of the program TOPAS (Coelho, 2018). The reasons are manifold. First of all, TOPAS is extremely fast and extremely robust, making it a great tool for beginners. It also tackles the different types of refinement problems (X-ray, neutron, fixed wavelength, time of flight, energy dispersive, structure solution, distortion modes, magnetic refinement, PDF analysis, multiple data sets and so on) that we think are most important. Our number one reason, however, is related to the unique scripting language of TOPAS, which allows experienced users to implement new developments in Rietveld refinement themselves. One example of this is the symmetry mode approach described in Chapter 8, which can be programmed without changing the TOPAS code (Campbell et al., 2007). The macro language of TOPAS also allows the implementation of new ideas by the user that can be rapidly shared with the entire user community (Scardi & Dinnebier, 2010). In this spirit we provide TOPAS code/macros for many of the corrections and algorithms described throughout the book. Many of these are available online at http://topas.dur.ac.uk/topaswiki/doku.php?id=book, so the reader can test the ideas. Most of the examples will work with any version of TOPAS, but some of the more advanced topics may only work with version 6 and above (Chapters 9–11, some of Chapter 12). Finally, the provision of standard macros via the topas.inc file acts as a wonderful “dictionary” detailing the mathematics behind many TOPAS commands.

It should be noted that we expect the reader to be familiar with the basics of crystallography and diffraction that are covered in many excellent introductory texts (e.g., Giacovazzo et al., 2011; Pecharsky & Zavalij, 2009; Gilmore et al. 2019). We have also kept the mathematical detail in the body of the text at the minimum level, which is necessary for understanding. Where more explanation is required we refer the reader to a stand-alone Chapter 13 that covers most of the higher mathematics needed to understand Rietveld refinement.

We would like to acknowledge Prof. Jörg Ihringer who gave permission for using his excellent script about diffraction for Chapter 13. Special thanks goes to Dr. Sebastian Bette for writing a major fraction of the chapter on “stacking faults.” We would also like to thank Prof. Branton Campbell and Dr Phil Chater for educating some of us through on-going collaborations in the areas of Chapters 8, 9 and 11.

Robert Dinnebier
Andreas Leineweber
John Evans
The book is dedicated to Alan Coelho (Brisbane) and Arnt Kern (Karlsruhe) for developing the unique TOPAS program and making it available to the powder diffraction community.

References


