R.E. Dinnebier & S.J.L. Billinge, "*Powder Diffraction – Theory and Practice*", RSC Publishing, 2008, pp. 153-159

Powder Diffraction
Theory and Practice

Edited by

Robert E. Dinnebier
Max-Planck Institute for Solid State Research, Stuttgart, Germany

Simon J. L. Billinge
Department of Physics and Astronomy, Michigan State University, USA

RSC Publishing

ISBN: 978-0-85404-231-9

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

When a peak is large, this may become quite significant,[114,115] including in the case of whole powder pattern decomposition detailed in the next section.

5.6 WHOLE POWDER PATTERN DECOMPOSITION (WPPD) – NO STRUCTURE

If the structure is used for the calculation of the intensities, then this is the whole powder pattern fitting (WPPF) Rietveld method for structure refinement (Chapter 13). In this section, it is considered that the structure is not used, but the indexing and the cell parameters are used. So, this is still WPPF but is the second variant, generally designated by WPPD (Whole Powder Pattern Decomposition). Clearly, any WPPF approach should be able to model the peak shape and width variation according to the diffraction angle. Again, this can be done either by fitting some analytical profile parameters in a semi-empirical approach, and the angular variation of these parameters is generally controlled by refining the U, W and W terms in the Cagliotti law[116] $(\mathrm{FWHM})^2 = U\tan^2\theta + V\tan\theta + W$, or using the FPA by ray-tracing.

5.6.1 No Cell Restraint

Obtaining all the peak positions, areas, breadths and shape parameters for a whole powder pattern without using the unit cell information is obviously limited to simple cases where there is not too much peak overlap. With such an approach one has to provide the number of peaks to be fitted so that the fit of an intricate group of peaks does not lead to large uncertainties if the cell is unknown. However, knowing the cell and space group and still using the peak position as a refinable parameter provides at least the correct number of peaks and an estimation of their starting position. Such calculations were made as an alternative to the Rietveld method, during the first stage of the so-called two-stage method for refinement of crystal structures.[117] In the case of X-ray data, early WPPF programs used profile shapes being a sum of Lorentzian curves,[118] or double-Gaussian.[119] The computer program PROFIT, deriving from a software for individual profile fitting[94] and extended to the whole pattern, was applied to the study of crystallite size and strain in zinc oxide[120] and for the characterization of line broadening in copper oxide.[121] Studying a whole pattern can also be done in simple cases by using software designed for the characterization of single or small groups of peaks, an example is a ZnO study[122] by using the computer program FIT (Socabim/Bruker). However, WPPD is mostly realized nowadays by using peak positions controlled by the cell parameters, even if the loss of that degree of freedom leads to slightly worst fits, increasing the profile *R* factors.

5.6.2 Cell-restrained Whole Powder Pattern Decomposition

Imposition of the peak positions calculated from a cell knowledge marked a great step in the quest for *ab initio* structure determination by powder

diffractometry (SDPD). Arguably, leaving free the peak positions will allow for taking account of subtle effects in position displacement (in stressed samples for example, Chapter 12). But variation with regard to the theoretical position as expected from cell parameters can be modeled as well in WPPD or the Rietveld method. Nowadays, two generic names are retained for such cell-constrained WPPD methods which can produce a set of extracted intensities suitable for attempting a structure solution; the Pawley and Le Bail methods. Both were derived from the Rietveld method.

5.6.2.1 The Pawley Method. Removing the crystal structure refinement in a Rietveld software, and adding the possibility to refine an individual intensity for every expected Bragg peak produced a new software (named ALLHKL) allowing the refinement of the cell parameters very precisely and the extraction of a set of structure factor amplitudes. The process was later called the Pawley method.[123] The least-squares ill-conditioning due to peak overlap was overcome by using slack constraints. The usefulness of that procedure for the confirmation of the cell indexing of a powder pattern of an unknown was completely obvious in this original paper. Nevertheless, no SDPD was realized by using the Pawley method before several years, probably because of the limitations in computer power. During these pioneering years, the version of ALLHKL could not extract the intensities for more than 300 peaks, so that for more complex cases it was necessary to divide the pattern into several parts. Moreover, it was a little difficult to avoid completely the under constrained nature of the problem due to peak overlap. Being successful provides equipartitioned intensities (*i.e.*, equal structure factors for those *hkl* Bragg peaks with exact overlap), but being unsuccessful could well produce negative intensities. Also, the first version applying Gaussian peak shapes could not produce any SDPD due to the relatively poor resolution of constant wavelength neutron data, and so it needed to be adapted to X-ray data, with the implementation of more complex peak shapes. A series of programs were proposed next, based on the same principles as the original Pawley method. Some programs were used to produce intensities to apply the so-called two-step-method for structure refinement, instead of using the Rietveld method (Cooper controversy[117]). Toraya introduced two narrow band matrices instead of a large triangular matrix, saving both computation time and memory space in his program WPPF.[124] Other program names are PROFIT,[125] PROFIN[126] (no slack constraints, but equal division of the intensity between expected peaks when the overlap is too close), FULFIT,[127] LSQPROF[128] and POLISH[129] (see also Chapter 17 for a snapshot of computer programs available at the time of printing). Improving the estimation of intensities of overlapping reflections in LSQPROF by applying relations between structure factor amplitudes derived from direct methods and the Patterson function was considered in a satellite program DOREES.[130] The question of how to determine the intensities of completely (or largely) overlapping reflections (systematic due to symmetry or fortuitous) in powder diffraction patterns cannot have a definite simple answer but continues to be much discussed since it is essential for improving our ability

DOCKET ALARM

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS
Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS
Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS
Sync your system to PACER to automate legal marketing.