1. INTRODUCTION

profile fitting following the Rietveld method can be carried out without a model, where the 'parameters' are the Bragg-peak intensities themselves; this is known as Pawley or Le Bail refinement, depending on details of the approach used (see Chapter 3.5). This allows more accurate determination of the structure factors from Bragg peaks in regions where there is significant peak overlap.

These days, with high-quality data from synchrotron X-ray sources and excellent algorithms (either direct methods or global-optimization methods in direct space), determination of even quite complex crystal structures from powder diffraction data is becoming a routine method in almost all branches of natural sciences and engineering. The success rate mainly depends on three parameters: the choice of measurement device, how well the pattern profile is described and how good the structure-solving algorithm is. It is becoming increasingly evident that the use of highly monochromatic parallel-beam synchrotron radiation is a huge advantage for obtaining accuracy in the atomic parameters, which allows for the interpretation of bonding and reaction mechanisms. In some cases, even details like rotational disorder can be extracted from powder diffraction data if maximum-entropy methods are combined with high-resolution synchrotron data.

1.1.6.2. *Local structure refinement*

As described in Section 1.1.5.3.2, similar full-profile-fitting strategies are now also carried out on total-scattering data that include diffuse-scattering intensity residing in what used to be considered as the 'background'. This is either done by taking a structural model, which may be similar to the crystal model used in the Rietveld method (but the crystallographic symmetry of the model could also be reduced) or be a discrete cluster or molecule. As with the Rietveld method, structural parameters are varied in such as way as to obtain a good fit of the calculated function to the measured one. These methods go beyond the average structure and yield information about the local structure in the material, which may be different from the long-range ordered (LRO) crystal structure (or indeed there may be no LRO structure, as is the case in liquids and glasses). They are becoming more popular as data quality and computational power increase.

Solving the structures of nanoparticles from PDF data is less well developed, although it has been demonstrated for some simple structures such as C_{60} and simple inorganic crystalline compounds. We expect that this will grow in importance in the coming years, following the trend of the Rietveld method and structure solution from powders.

1.1.6.3. *Parametric Rietveld refinement*

The conventional approach to analysing a set of powder patterns is to treat each powder pattern independently, thus refining the entire set of all relevant parameters for each pattern separately. Further analysis of the values of these parameters, for example fitting with empirical or physics-based functions such as fitting the temperature dependence of the ADPs with a Debye model, is then performed after the Rietveld refinements. Alternatively, all powder patterns can be subjected to refinement simultaneously, which allows the refinement of the functional dependence of external variables instead of deriving the parameters of the function from the individual Rietveld refinements afterwards. This so-called parametric or surface Rietveld refinement was first introduced by Stinton & Evans (2007). Parametric refinement offers several advantages over the traditional

sequential refinement approach because the correlation between parameters and the final standard uncertainty can be reduced by introducing simple and physically meaningful constraints and restraints. Furthermore, it is possible to refine noncrystallographic parameters such as rate constants or temperatures directly from Rietveld refinement (Stinton & Evans, 2007). Of course, introducing external constraints in this way may introduce bias into the refinement if the constraint is not valid. For example, if there is anharmonicity in the motion and the temperature dependence of the ADPs does not follow the Debye law, carrying out a parametric refinement where the Debye law is presumed will result in biased refinements. However, with careful application, this is a potentially powerful approach to maximizing the quantitative information available from powder data in complex systems. In the following, the basic concept of parametric refinement is illustrated with several examples.

If we assume a set of p_{max} powder patterns from a single sample that have been measured as a function of the value of an external variable, *e.g.* time, temperature or pressure, equation (1.1.92) can be formally written for each powder pattern separately:

$$Y\text{calc}_{i,\text{pattern}(1)} = \text{function}(p_{1,\text{pattern}(1)}, p_{2,\text{pattern}(1)}, \ldots, p_{m,\text{pattern}(1)})$$
$$Y\text{calc}_{i,\text{pattern}(2)} = \text{function}(p_{1,\text{pattern}(2)}, p_{2,\text{pattern}(2)}, \ldots, p_{m,\text{pattern}(2)})$$
$$Y\text{calc}_{i,\text{pattern}(p_{max})}$$
$$= \text{function}(p_{1,\text{pattern}(p_{max})}, p_{2,\text{pattern}(p_{max})}, \ldots, p_{m,\text{pattern}(p_{max})}).$$
(1.1.93)

If a functional dependency of some of the parameters p on external variables T exists, these parameters may be expressed as functions of these variables, for example T. This functional relationship can be used to constrain together the p parameters for individual patterns measured at different temperatures, drastically reducing the number of global parameters. Equation (1.1.93) can thus be written as

$$Y\text{calc}_{i,\text{pattern}(1)}$$
$$= \text{function}(p_{1,\text{pattern}(1)}, p_{2,\text{pattern}(1)} = f(T_1, T_2, \ldots, T_t), \ldots, p_{m,\text{pattern}(1)})$$
$$Y\text{calc}_{i,\text{pattern}(2)}$$
$$= \text{function}(p_{1,\text{pattern}(2)}, p_{2,\text{pattern}(2)} = f(T_1, T_2, \ldots, T_t), \ldots, p_{m,\text{pattern}(2)})$$
$$\vdots$$
$$Y\text{calc}_{i,\text{pattern}(p_{max})}$$
$$= \text{function}(p_{1,\text{pattern}(p_{max})}, p_{2,\text{pattern}(p_{max})} = f(T_1, T_2, \ldots, T_t),$$
$$\ldots, p_{m,\text{pattern}(p_{max})}).$$
(1.1.94)

The cost function (1.1.91) to be minimized changes accordingly:

$$R_w = \sum_{\text{pattern}=1}^{p_{max}} \left(\sum_{i=0}^{n-1} \left(w_{i,\text{pattern}} \left(Y\text{obs}_{i,\text{pattern}} - Y\text{calc}_{i,\text{pattern}} \right)^2 \right) \right).$$
(1.1.95)

1.1.7. Outlook

As is evident from the above, the information content in a powder diffraction pattern is enormous. This chapter gives only an overview of the types of information about materials that can be obtained from powder diffraction data, and the various approaches mentioned here are described in greater detail in the rest of this volume. The powder community is growing, as is the number of applications of powder diffraction in all the materials

 references