

### 3.4. Indexing a powder diffraction pattern

A. ALTOMARE, C. CUOCCI, A. MOLITERNI AND R. RIZZI

#### 3.4.1. Introduction

The crystal structure solution process presupposes that the crystal cell and the space group are known. In other words, the first step in the solution pathway is the identification of the unit-cell parameters. Knowledge of the crystal structure strongly depends on the determination of the cell: a cell incorrectly defined does not lead to the solution. The cell-determination process (which operates in a 6-dimensional continuous parameter space) is also called ‘indexing’ because it consists of assigning the appropriate triple ( $hkl$ ) of Miller indices of the lattice plane to each of the  $N_1$  experimental diffraction lines (in a  $3N_1$ -dimensional integer-valued index space) (Shirley, 2003). (In this chapter, ‘line’ and ‘peak’ are used synonymously.) In the case of powder diffraction, the determination of the cell parameters is not a trivial task, and it is much more difficult than in the single-crystal case. This is because the information about the three-dimensional reciprocal space is compressed into the one-dimensional experimental powder pattern. Whatever the method used, working in the parameter or index space, powder pattern indexing aims to recover the three-dimensional information from the positions of the diffraction peaks in the observed profile. In particular, the experimental information used for carrying out the indexing process is the  $d_{hkl}$  interplanar spacings, which are related to the diffraction angles by the well known Bragg law:

$$2d_{hkl} \sin \theta_{hkl} = \lambda.$$

In theory, if we had available an experimental pattern at infinite resolution with well resolved peaks with no overlapping, the determination of the six cell parameters corresponding to a problem with six degrees of freedom would be easy (Shirley, 2003). In practice, only the first 20–30 observed lines are useful for two main reasons: (1) they are less sensitive to small changes in the cell parameters than the higher-angle lines; and (2) higher-angle lines (even if they seem to be single peaks) actually often consist of more than one overlapping peak and their positions cannot be accurately evaluated. Using higher-angle lines is therefore unwise. The successful outcome of powder pattern indexing is correlated to which and how many  $d_{hkl}$  values derived from the peaks in the diffraction pattern are selected and how reliable they are. Precision and accuracy in detecting peak positions are essential conditions for successful indexing (Altomare *et al.*, 2008). Unfortunately they can be degraded by different sources of errors: peak overlap, poor peak resolution,  $2\theta$  zero shift, errors in measurement, and a low peak-to-background ratio. Moreover, impurity lines (*i.e.* peaks from a different chemical phase in the sample to the compound being studied) can hinder the attainment of the correct result. The history of indexing, having its origin in the early 20th century (Runge, 1917), has produced several methods and software packages (Shirley, 2003; Werner, 2002) with surprising progress in strengthening and automating the cell-determination process. Innovative approaches that aim to reduce the dependence on the  $d_{hkl}$  values (by avoiding the peak-search step and considering the full information contained in the diffraction pattern) have also been developed. Despite great advances, powder pattern

indexing is still a challenge in many cases. Factors that affect the success or failure of the process include: the presence of diffraction peaks from unexpected phases, the precision in the peak-position value, the size of the unit cell to be identified (indexing is easier if the unit cell is not too big) and the symmetry (indexing a pattern from a compound with high symmetry is generally more reliable than for a compound with lower symmetry). Before the zeroth step of the indexing process (the searching for peaks in the experimental pattern) it is always necessary to obtain good-quality diffraction data. Of course, the use of synchrotron radiation is preferable, but conventional laboratory X-ray data are usually suitable. Whether automated or manual, the peak search and each successive step of the indexing process must be carefully checked. For example, in a first attempt the positions that correspond to overlapping peaks could be set aside. If one attempt fails, the most useful tactic is to try another software package, since the programs available at present are based on different approaches.

The aim of this chapter is first to illustrate the background of the topic and the main theoretical approaches used to carry out the powder pattern indexing, and then to give some examples of applications. Section 3.4.2 is mainly devoted to the basic concepts of a crystalline lattice, the main indexing equations and figures of merits; Section 3.4.3 discusses the traditional and non-traditional methods developed for indexing a powder pattern, and Section 3.4.4 discusses some applications, referring to the most widely used indexing programs.

#### 3.4.2. The basic concepts of indexing

We now describe some concepts that are fundamental in crystallography and useful for understanding the indexing process. The measured diffraction intensities correspond to the reciprocal-lattice points

$$\mathbf{r}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$

The Miller indices ( $hkl$ ) identify the plane of the direct lattice and  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  are the three vectors of the reciprocal lattice, which are related to the direct lattice by

$$\mathbf{a} = \frac{\mathbf{b}^* \times \mathbf{c}^*}{V^*}, \quad \mathbf{b} = \frac{\mathbf{c}^* \times \mathbf{a}^*}{V^*}, \quad \mathbf{c} = \frac{\mathbf{a}^* \times \mathbf{b}^*}{V^*},$$

where

$$V^* = \mathbf{a}^* \cdot \mathbf{b}^* \times \mathbf{c}^*$$

is the reciprocal-cell volume ( $V^*$  is the inverse of the direct-unit-cell volume  $V$ ).

In case of single-crystal data, the three-dimensional nature of the experimental diffraction data makes it easy to identify  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$ , from which the direct-space unit-cell vectors are derived (Giacovazzo, 2011).

In case of powder diffraction, the three-dimensional nature of the diffraction data is compressed into one dimension in the experimental pattern, and the accessible experimental information is the  $d_{hkl}$  values involved in the Bragg law and related to the