

# Structure determination from powder diffraction data: an overview

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## 2.1 Introduction

The explosion of interest in powder diffraction methods during the last 30 years has been driven by a number of factors. The major one was most certainly the development of the Rietveld method (Rietveld 1969) in the late 1960s, since, at a stroke, this extended the scope of powder techniques from simple, high-symmetry materials to compounds of substantial complexity in any space group. Within five years, for example, the method was being used to refine the structures of orthorhombic and monoclinic materials with as many as 22 atoms in the asymmetric unit (Von Dreele and Cheetham 1974), and by 1977, Cheetham and Taylor were able to review the application of the Rietveld method to over 150 compounds (Cheetham and Taylor 1977). The majority of these early applications involved the use of neutrons, but the field received a further boost in the late 1970s and early 1980s with the extension of the Rietveld method to X-ray data (Malmros and Thomas 1977; Young *et al.* 1977), time-of-flight neutron data (Von Dreele *et al.* 1982), and then synchrotron X-ray data (Cox *et al.* 1983). These instrumental advances were accompanied by software developments, such as the availability of the DBWS (Wiles and Young 1981) and GSAS (Larson and Von Dreele 1987) packages, making possible the analysis of data from complex mixtures or the simultaneous analysis of more than one dataset. Another major area of interest has been the development of methods for solving unknown structures from powder diffraction data, a subject that is the primary focus of this book.

The developments in powder diffraction have been driven by a growing need for tools that are able to probe the structures of materials that are only available in powder form, or can only be studied as powders (e.g. under difficult *in situ* conditions). Such materials include many zeolite catalysts, as well as certain high  $T_c$  cuprates and fullerenes. Table 2.1 lists some of the many areas in which powder diffraction methods have had a major impact; clearly, modern materials science and many other areas have been major beneficiaries of the developments in this area during the last 30 years, and this trend will surely continue well into the twenty-first century.

**Table 2.1** Impact of powder diffraction methods in materials science and other areas

Hydrogen storage	Superconductivity
Metal hydrides	High $T_c$ cuprates
Magnets	Batteries/fuel cells
Magnetoresistance, GMR	$\beta$ -alumina solid electrolytes
Heterogeneous catalysts	Ferroelectrics
Zeolites, clays	PbTiO <sub>3</sub> etc.
Ceramics	Electro-optics
Zirconias	Non-linear optics, e.g. KTiOPO <sub>4</sub>
Novel materials	Biominerals
C <sub>60</sub> fullerenes	Apatites
Coordination compounds	Organic materials
Homogeneous catalysts	Pharmaceuticals

The aim of this overview is to trace the key developments in powder diffraction methods from their discovery in the early twentieth century to the present day. The evolution of tools for solving unknown structures will be emphasized, while remembering, of course, that the refinement step is also an important component of this process.

## 2.2 Early history of powder diffraction

The possibility of using powder diffraction methods to study materials was recognized shortly after the discovery of X-ray diffraction by Laue and von Knipping in 1910. In particular, the construction of a simple powder diffractometer was described by Hull in 1917 (Hull 1917), and the instrument was used to obtain patterns from a number of simple materials such as diamond, graphite and iron. Even at this early stage, the use of metal foils to remove  $K\beta$  radiation from the X-ray beam was well understood. Within a few years, many others, including the Braggs and Pauling, had exploited the powder method to study a wide range of materials, including metals, minerals, and simple organic solids. It could reasonably be argued that the first *ab initio* structure determinations were performed during this period, since the crystal structures of many simple materials (e.g. rocksalt) were obtained from powder diffraction data alone.

The first systematic attempts to determine unknown structures of non-cubic materials were probably those of Zachariasen, reported in the late 1940s. For example, the hexagonal structure of UCl<sub>3</sub>, in space group  $P6_3/m$ , was determined by first placing the heavy atom and then estimating the position of the chlorine by careful inspection of the intensities of different classes of reflections (Zachariasen 1948a). In the same issue of *Acta Crystallographica*, a series of

papers by Zachariasen describe the structures of eight uranium halides and oxohalides from X-ray powder data (Zachariasen 1948*b*), and in the following year a similar approach was used by Mooney to solve the tetragonal structure of  $\text{UCl}_4$  (Mooney 1949).

These early approaches might be regarded as trial-and-error methods, though they reveal great insight into the relationships between trends in the integrated intensities of different classes of reflections and the locations of the scattering centres. They certainly laid the foundations for the systematic approaches that evolved during subsequent decades.

### 2.3 Early *ab initio* approaches

There are at least two papers in the 1960s that describe systematic attempts to use the structure-solving tools of modern crystallography, Direct methods and Patterson techniques, to solve structures from powder data. In a remarkable paper by Zachariasen and Ellinger (1963), the monoclinic structure of  $\beta$ -plutonium, in space group  $I2/m$ , was solved by using a manual Direct methods phasing procedure. There are seven Pu atoms in the asymmetric unit, underlining the complexity of this task. A particularly interesting aspect of this work was the clever use of the anisotropic thermal expansion of  $\beta$ -plutonium to unscramble the individual Bragg intensities of overlapping reflections from patterns collected at different temperatures (see Chapter 9). As will become clear later, the treatment of overlapping reflections remains one of the major issues in structure determination from powder data.

Another eye-catching paper from the 1960s is that by Debets (1968) in which the orthorhombic structure of  $\text{UO}_2\text{Cl}_2$  in space group  $Pnma$  was determined by Patterson methods. As in the work of Zachariasen and Ellinger, their approach is not radically different from that which has been used widely in the late 1980s and 1990s. An interesting difference between these early studies and the more recent work, however, is that the structure refinement step did not take advantage of least-squares methods, which, of course, are used routinely today. Nevertheless, the essential correctness of the  $\text{UO}_2\text{Cl}_2$  structure has since been confirmed by Taylor and Wilson (1973).

### 2.4 Pre-Rietveld refinement methods

The development of least-squares crystallographic structure-refinement methods in the 1960s, which was facilitated by the growing availability of digital computers, was applied not only to single-crystal data but also to powder data. A number of laboratories, such as UKAEA, Harwell, made widespread use of single-crystal codes for refining structures from powder data, and some of the codes were adapted to handle groups of non-equivalent overlapping reflections that could not be resolved experimentally. Table 2.2 shows an example of such a

**Table 2.2** Integrated-intensity structure refinement for  $\text{Fe}_{0.923}\text{O}$  at  $800^\circ\text{C}$ , based upon powder neutron diffraction data. There were 12 observations and four variable parameters: the scale factor, the occupancy number for the tetrahedral interstitial site, and independent isotropic temperature factors for the iron and oxygen atoms (Cheetham *et al.* 1970). The  $R_I$  value is 0.78 per cent

hkl	I(obs)	I(calc)
111	6092	6315
200	89 766	89 604
220	79 186	79 285
311	3378	3484
222	26 340	26 139
400	12 697	13 094
331	1540	1377
420	31 104	31 301
422	23 695	23 438
333/511	1061	898
440	5831	6042
600/442	10 394	10 308

refinement, carried out at Harwell shortly before a Rietveld program that would run on the computer there became available. The paucity of data and the poor observation-to-parameter ratio make it hard to believe that this was essentially the state-of-the-art in the late 1960s, but it is important to stress that such studies played an important role at the time in the quantitative structural characterization of high-symmetry inorganic materials. A particular class of materials that benefited from this approach was that of non-stoichiometric compounds, which are typically high-symmetry phases that are found at high temperatures. Nevertheless, the limitation of the integrated intensity method, at the time, was that it could not be applied to the complex patterns obtained from low-symmetry materials. The advent of the Rietveld refinement method, however, was soon to solve this problem.

## 2.5 Rietveld refinement

In response to the need to develop enhanced procedures for obtaining structural information from powder samples, in the late 1960s, Rietveld (1969) proposed a method for analysing the more complex patterns obtained from low-symmetry materials by means of a curve-fitting procedure. The least-squares refinement minimizes the difference between the observed and calculated profiles, rather

than individual reflections. In the first instance, this procedure was carried out with constant wavelength neutrons, rather than X-rays, because of the simpler peak shape of the Bragg reflections. With constant wavelength neutrons, it can normally be assumed that the reflections are Gaussian in shape, and the calculated intensity at each point (say,  $0.05^\circ 2\theta$  steps) on the profile is obtained by summing the contributions from the Gaussian peaks that overlap at that point. In addition to the conventional parameters in the least-squares procedure (i.e. scale factor, atomic coordinates and temperature factors), additional parameters are required: the lattice parameters (which determine the positions of the reflections), a zero-point error for the detector, and three parameters that describe the variation of the Gaussian half-width (full width at half maximum intensity) with scattering angle. The technique has been applied to a wide range of solid-state problems and has been reviewed by several authors during the last 25 years (Cheetham and Taylor 1977; Hewat 1986; Young 1993).

The application of the Rietveld method to neutron data in the early 1970s was soon followed by its extension to laboratory X-ray diffractometer data (Malmros and Thomas 1977; Young *et al.* 1977). The problem of the more complex peak shape was resolved by employing alternative peak-shape functions, such as the Lorentzian and the pseudo-Voigt. Other problems that can plague X-ray studies include preferred orientation and poor powder averaging (graininess), both of which arise from the fact that X-rays probe a smaller sample volume than do neutrons; these were addressed by paying closer attention to the data collection strategy.

The accuracy and precision of a structure refinement from X-ray data can normally be optimized by collecting high-resolution data at a synchrotron source (Cox *et al.* 1983). The resolution of the powder diffractometers at second and third generation sources is so good that sample imperfections now play a major role in determining the shape of the Bragg peaks. This presents both challenges and opportunities. For the crystallographer, the subtle variations in peak shape from one class of reflection to another (which may stem from, say, anisotropic particle size or strain effects) may be an irritation if the sole aim is to obtain a high-quality refinement of the crystal structure. However, the materials scientist may be delighted to retrieve a wealth of additional information pertaining to the microstructure of the sample.

Refinement by the Rietveld method is now commonplace with both laboratory and synchrotron X-ray data, although it is not, in general, as precise as the neutron method (Table 2.3). There are three reasons for this. First, as mentioned above, it is more difficult to collect X-ray data that are essentially free from systematic errors. Consequently, it is not unusual to find that the precision, as measured in terms of the estimated standard deviations (e.s.d.s), gives a misleading impression of the real accuracy of the structure. Second, the fall-off of intensity with scattering angle due to the X-ray form factor reduces the quality of the information that can be retrieved from the high-angle region of an X-ray pattern. Third, the wide variation in X-ray scattering factors between

elements from different parts of the periodic table leads to considerable differences in the sensitivities with which atoms can be located; in particular, heavy atoms will be better defined than light atoms. In Table 2.3, for example, the  $y$  coordinate of Cr(2) is determined with greater precision than the  $y$  coordinate of O(2) by X-ray powder diffraction. This problem does not arise to the same extent with neutrons because their scattering amplitudes (or scattering lengths, as they are known) fall within a relatively narrow range of values (Bacon 1975).

The Rietveld method was also extended to the analysis of time-of-flight neutron powder data collected at pulsed sources. The procedure is essentially the same as that used in constant-wavelength experiments, except that the peak shape function is considerably more complex, due in part to the shape of the neutron pulse, and wavelength-dependent corrections (e.g. absorption and extinction) must be taken into account (Von Dreele *et al.* 1982). One advantage

**Table 2.3** Structural parameters for  $\alpha$ -CrPO<sub>4</sub> refined using synchrotron X-ray (marked X) and neutron (N) data in *Imma* with e.s.d.s in parentheses (Attfield *et al.* 1988). Values from the reported single-crystal study (marked S) are given for comparison (Glaum *et al.* 1986)

Atom	$x$	$y$	$z$	$B_{iso}$ <sup>a</sup>
Cr(1)	1/2	1/2	0	0.3(2)N 0.283(6)S
Cr(2)	1/4	0.3660(3)X 0.3650(4)N 0.36611(3)S	1/4	0.0(1)N 0.316(4)S
P(1)	1/2	1/4	0.0819(12)X 0.0790(8)N 0.0825(2)S	0.0(1)N 0.30(1)S
P(2)	1/4	0.5738(4)X 0.5739(2)N 0.57358(5)S	1/4	0.47(8)N 0.345(7)S
O(1)	0.3790(10)X 0.3766(3)N 0.3773(2)S	1/4	0.2269(17)X 0.2280(5)N 0.2268(3)S	0.53(8)N 0.42(2)S
O(2)	0.3603(6)X 0.3610(2)N 0.3611(1)S	0.4914(5)X 0.4907(1)N 0.4902(1)S	0.2145(11)X 0.2142(3)N 0.2146(2)S	0.62(6)N 0.42(1)S
O(3)	0.2263(6)X 0.2240(1)N 0.2238(1)S	0.6352(5)X 0.6368(2)N 0.6363(1)S	0.0576(10)X 0.0546(3)N 0.0552(2)S	0.68(5)N 0.56(1)S
O(4)	1/2	0.3509(8)X 0.3486(2)N 0.3496(2)S	-0.0457(15)X -0.0422(4)N -0.0432(3)S	0.31(7)N 0.50(2)S

<sup>a</sup>For the powder X-ray refinement, overall  $B_{iso} = 0.24(7) \text{ \AA}^2$

of time-of-flight powder methods is that the whole diffraction pattern is collected simultaneously since the counter, or bank of counters, remains stationary, making it an attractive way of following structural changes that evolve as a function of time, temperature or pressure. In addition, since the incident and scattered beams can pass through small apertures in, say, a high-pressure apparatus, the design of special environments is clearly easier for such measurements (Jorgensen 1988). A further advantage is that it is relatively easy to obtain high-resolution data by using a long incident flight path and placing the detectors in the back scattering position.

The Rietveld method is a powerful tool, but it is limited by the same drawback that affects powder methods in general: the loss of information that arises from the compression of the three-dimensional diffraction pattern into a single dimension. It is also important to underline the fact that the Rietveld method, though an excellent technique for *refining* structures, requires a good starting model if it is to converge successfully and does not, by itself, constitute a method for *structure determination*. We shall now return to the question of solving unknown structures and examine the state-of-the-art in this area.

## 2.6 Solving unknown structures from powder data

There has been a great deal of interest concerning the determination of unknown structures from powder diffraction data during the last decade and there have been several reviews of the subject (Cheetham 1986; Cheetham 1993; Harris and Tremayne 1996). The process may conveniently be broken down into a series of steps, though there may be considerable overlap between the different stages:

- (1) determination of the unit cell;
- (2) decomposition of the powder pattern into integrated intensities,  $I_{hkl}$ ;
- (3) assignment of space group from systematic absences;
- (4) solution of the phase problem;
- (5) refinement of the structure, typically by the Rietveld method.

Most of these stages are discussed in detail in more specialized chapters in this book, so only a few general comments will be made at this stage.

Step 1, the indexing of the powder pattern to yield a unit cell, is normally carried out by autoindexing methods, for which a number of powerful computer programs are now available (see Chapter 7). These include ITO (Visser 1969), TREOR (Werner *et al.* 1985) and DICVOL (Boultif and Louër 1991). Access to more than one of these programs is desirable since they work in different ways and successful indexing may not always be achieved with one particular program; the key point is that successful indexing is facilitated by collecting high-quality data. In practice, with careful instrument alignment, careful data collection and accurate peak-position determination, it seems that few structure

determinations stumble at the point of determining the unit cell. Of course, as mentioned in Section 1.2 of Chapter 1, this situation may well change.

We should also note that the identity of the space group may become apparent following the autoindexing stage, though uncertainties frequently remain and must be resolved at a later stage (see below). In cases where the unit-cell determination is proving difficult, it might be worthwhile to obtain selected area electron diffraction patterns from microcrystals, noting that an electron diffraction pattern is the equivalent of a zero-level precession photograph with X-rays. The feasibility of this approach will depend upon the stability of the sample in the beam, but the extra effort that it entails may be rewarded, especially if there is a subtle superstructure to which powder X-ray methods may not be sensitive.

The second step of the structure determination, the decomposition of the pattern into individual integrated intensities, is often the most challenging one because it is here that severe ambiguities may arise due to overlapping of peaks (see Chapter 8). Such overlapping may be accidental or may be an unavoidable consequence of the symmetry (e.g. the exact overlap of non-equivalent reflections in certain high-symmetry Laue groups). A number of powerful single-step strategies that have been developed to address the pattern-decomposition problem are now embodied in computer programs such as ALLHKL (Pawley 1981), WPPF (Toraya 1986), GSAS (Larson and Von Dreele 1987, incorporating the Le Bail method (Le Bail *et al.* 1988)), LSQPROF (Jansen *et al.* 1992a) and EXTRA (Altomare *et al.* 1995). The earliest development in this area, due to Pawley (1981), was based upon a Rietveld fitting procedure in which the integrated intensities were refined in addition to the lattice parameters, peak-shape parameters, etc. Le Bail's method is closely related, but is somewhat more robust in its treatment of overlapping data.

From this stage onwards, the analysis can mirror that of a single-crystal study. In stage 3, the possible space groups can be assigned from the systematic absences, although in cases of uncertainty it may be useful to carry out the pattern decomposition in a number of alternative space groups (or to obtain a series of electron diffraction patterns, as discussed above). Uncertainties often remain (as they do with single-crystal methods) and may have to be resolved during the structure solution and/or refinement steps. The phase problem is then solved in stage 4 by conventional crystallographic methods, that is, Patterson or Direct methods, the choice being dictated by the chemical nature of the material. Early work in this area utilized programs that had been developed for the analysis of single-crystal data, but some Direct methods codes that are optimized for powder data are now available, including EXPO (Altomare *et al.* 1999) and SIMPEL (Jansen *et al.* 1993) (see Chapters 10 and 11). Patterson determinations are also benefiting from vector-search algorithms (see Chapters 12 and 13).

As with the solution of structures from single-crystal data, light atom problems will normally respond better to Direct methods, while structures containing a subset of heavy atoms will be more amenable to Patterson

techniques. The principal difficulty is that, even if there are no ambiguities due to peak overlap, the data set will be considerably smaller than that obtained in a single-crystal study and the phasing procedure will be less straightforward. It is a tribute to the robustness of modern structure-solving techniques that it is still possible to determine structures under these unfavourable circumstances. Once a suitable starting model has been obtained, stage 5, the refinement of the structure, can proceed by using the Rietveld method. Quite commonly, the starting model will be incomplete and additional atoms will be found during the refinement procedure by using difference Fourier methods.

More recently, the probability of solving a structure from powder data has improved because there has been a move towards the development of pattern-decomposition methods that are more sophisticated. Typically, these new methods are not single-step procedures, but involve an iteration between the pattern-decomposition step and the subsequent Patterson or Direct methods calculations. For example, the observed intensities that are obtained from a successful pattern decomposition should yield a Patterson map that fulfils certain requirements; for example, it should be positive at all points. Some of the codes that link the pattern decomposition and the structure-solving stage are DOREES (Jansen *et al.* 1992b) and FIPS (Estermann *et al.* 1992; Estermann and Gramlich 1993), and those based upon maximum entropy (David 1987, 1990) and Bayesian fitting procedures (Sivia and David 1994). A potentially powerful approach is the use of entropy maximization and likelihood ranking (Bricogne and Gilmore 1990; Gilmore *et al.* 1993), a method that has been used in other areas of crystallography and has now been adapted for powder data in the MICE computer program (Gilmore *et al.* 1990; see also Chapter 14).

## 2.7 Trial-and-error and simulation methods

In addition to the systematic approaches described above, there has been a long-standing tradition of solving unknown structures from powder data by trial-and-error methods. A typical example can be seen in the work of Titcomb *et al.* (1974), who solved the superstructure of the metal hydride phase,  $\text{CeH}_{2+x}$ , by exploring all of the possible arrangements of the interstitial hydrogens in the fluorite-related parent structure. The fluorite-related structure of  $\text{Bi}_3\text{ReO}_8$  was solved in a similar manner (Cheetham and Rae Smith 1985). The starting models obtained by trial-and-error were then refined by the Rietveld method. In this approach, it is clearly advantageous (and often essential) to use information that may be available from other studies on the material of interest. In  $\text{Bi}_3\text{ReO}_8$ , for example, it was known from infra-red measurements that the oxygen coordination around the rhenium atom was tetrahedral. Similarly, model-building, together with information from electron microscopy and  $^{29}\text{Si}$  magic angle spinning NMR, was used to elucidate the structure of the molecular sieve zeolite, ZSM-23 (Wright *et al.* 1985).

The manual trial-and-error strategy is not very attractive, since it can be very time-consuming and the chances of success are not particularly high. However, modern simulation methods, together with the power of modern computers, can be used to remove much of the labour and uncertainty from this approach by automating the way in which previous knowledge of a system, or related systems, is used. In the zeolite area, for example, Deem and Newsam (1989) have developed a simulated annealing method that can be used to predict unknown zeolite structures from a knowledge of the unit cell, the space group, and the number of tetrahedral Si/Al (T) sites in the cell. In cases where the space group or number of T sites is uncertain, the calculation is sufficiently fast for alternative possibilities to be tested. The simulation procedure employs cost functions that depend upon the T–T distances and T–T–T angles in a large body of known zeolitic structures. Further refinement of this approach involving the implementation of a biased Monte Carlo scheme was reported recently (Falcioni and Deem 1999).

Molecular crystals, too, lend themselves naturally to simulation methods, since their molecular structures (or fragments thereof) are often known with some confidence. We can use prior knowledge of the molecular structure (or an energy-minimized molecular structure obtained by quantum mechanical calculations) and move the molecular fragment by translations and rotations within the unit cell using algorithms ranging from simple grid search to simulated annealing and genetic algorithms (see Chapters 15 and 16). Knowledge of the space group is again required, of course. The crystal structure can be predicted by using energy functions based upon appropriate inter- and intra-molecular potentials, or by comparison between the calculated and observed X-ray powder patterns. Approximate models can then be refined by the Rietveld method. Examples of structures solved in this manner include piracetam,  $C_6H_{10}N_2O_2$  (Louër *et al.* 1995) and 1-methylfluorene,  $C_{14}H_{12}$  (Tremayne *et al.* 1996). The approach is very straightforward for rigid molecules, but becomes considerably more difficult as the number of degrees of freedom increases. Nevertheless, algorithmic developments have led to a situation where the crystal structures of relatively flexible molecular moieties can be solved quite straightforwardly (see Section 2.8 and Chapters 15 and 16).

## 2.8 Some examples of structure determination from powder data

A great deal of the development work in the field of structure determination from powder data has relied on the use of conventional, laboratory X-ray sources, and there were a number of important early successes in the area (Berg and Werner 1977; Clearfield *et al.* 1984). However, synchrotron X-ray data has profound advantages over conventional X-ray data for structure determination. In particular, the combination of the high brightness and excellent vertical collimation can be harnessed to construct diffractometers with unparalleled

angular resolution, as in the case of the instrument at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Cox *et al.* 1986), where the resolution at the focusing position is  $<0.02^\circ$  in  $2\theta$ . This is partly achieved by constructing the instrument in the vertical plane, since the vertical divergence,  $\theta_v$ , is only  $\sim 0.01^\circ$  at 2.5 GeV. With high-resolution data, the solution of structures from powder data is greatly facilitated because ambiguities due to peak overlap are minimized and the information content of the dataset is optimized. Many successful structure solutions and refinements have now been performed, a selection of which is given in Table 2.4. On the other hand, relatively few structures have been solved from powder neutron diffraction data. This is partly a consequence of the lower resolution of most neutron diffractometers, but it is mainly due to the near equivalence of the neutron scattering lengths for most elements, as a result of which the phase problem cannot be solved on the basis of locating a small subset of atoms. Some recent examples of structure solutions from neutron diffraction data, obtained by the application of both Direct methods and global optimization strategies, are discussed in Chapter 5.

**Table 2.4** Some examples of *ab initio* structure determinations from synchrotron X-ray powder data

Compound	Space group	No. of atoms in asymmetric unit	Ref.
$\alpha$ -CrPO <sub>4</sub>	<i>Imma</i>	8	1
I <sub>2</sub> O <sub>4</sub>	<i>P2<sub>1</sub>/c</i>	6	2
Al <sub>2</sub> Y <sub>4</sub> O <sub>9</sub>	<i>P2<sub>1</sub>/c</i>	15	2
MnPO <sub>4</sub> · H <sub>2</sub> O	<i>C2/c</i>	6	3
PbC <sub>2</sub> O <sub>4</sub>	<i>P1</i>	7	4
Clathrasil, Sigma-2	<i>I4<sub>1</sub>/amd</i>	17	5
LaMo <sub>5</sub> O <sub>8</sub>	<i>P2<sub>1</sub>/a</i>	14	6
BeH <sub>2</sub>	<i>Ibam</i>	4	7,8
UPd <sub>2</sub> Sn	<i>Pnma</i>	4	9
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	<i>Pna2<sub>1</sub></i>	19	10
NaCD <sub>3</sub>	<i>I222</i>	10	11
C <sub>10</sub> N <sub>6</sub> SH <sub>16</sub>	<i>P2<sub>1</sub>/n</i>	33	12
BaBiO <sub>2.5</sub>	<i>P2<sub>1</sub>/c</i>	5	13
(VO) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · 9H <sub>2</sub> O	<i>P2<sub>1</sub>/n</i>	13 non-H	14
CuPt <sub>3</sub> O <sub>6</sub>	<i>Pn2<sub>1</sub>m</i>	10	15
Ga <sub>2</sub> (HPO <sub>3</sub> ) <sub>3</sub> · 4H <sub>2</sub> O	<i>P2<sub>1</sub></i>	29	16
La <sub>3</sub> Ti <sub>5</sub> Al <sub>15</sub> O <sub>37</sub>	<i>Cc</i>	60	17

1 = Attfield *et al.* 1986; 2 = Lehmann *et al.* 1987; 3 = Lightfoot *et al.* 1987; 4 = Christensen *et al.* 1989; 5 = McCusker 1988; 6 = Hibble *et al.* 1988; 7 = Smith *et al.* 1987; 8 = Smith *et al.* 1988; 9 = Marezio *et al.* 1988; 10 = Kurahshi *et al.* 1989; 11 = Weiss *et al.* 1990; 12 = Cernik *et al.* 1991; 13 = Lightfoot *et al.* = 1991; 14 = Teller *et al.* 1992; 15 = Hriljac *et al.* 1991; 16 = Morris *et al.* 1992; 17 = Morris *et al.* 1994

In the first example of a structure solved from synchrotron X-ray powder data, carried out in 1986 by Attfield *et al.* (1986), the orthorhombic structure of  $\alpha$ -CrPO<sub>4</sub>, with eight atoms in the asymmetric unit, was solved by Patterson methods using a vector-search procedure; 68 well-resolved peaks were utilized. A relatively poor  $R_p$ -factor (19.3 per cent) was obtained for the final Rietveld refinement with the synchrotron data, no doubt due to problems with preferred orientation and  $hkl$ -dependent line-broadening effects, but a subsequent medium resolution neutron study (on D1a at ILL Grenoble) gave an excellent fit ( $R_p = 8.3$  per cent), confirming the correctness of the X-ray model. A comparison of the coordinates obtained from the X-ray and neutron refinements, and a subsequent single-crystal study, was given in Table 2.3. In particular, we note that the neutron refinement gives improved precision for almost all atoms, in spite of the modest resolution of the neutron data.

During the last decade, there has been widespread use of synchrotron powder methods to solve unknown structures (Table 2.4), the most striking development being the extension of the method to systems of very considerable complexity, with as many as 60 atoms in the asymmetric unit of the cell (Morris *et al.* 1994). Such complex structures normally require a combination of both synchrotron X-ray and neutron data for their solution and refinement, since they lie at the limit of what can currently be done with a single dataset. With the advent of global optimization methods, challenging 'equal atom' organic structures are also being solved. However, subsequent refinement is not trivial. Some recent examples include forms A and B of famotidine and the nitrate and acetate salts of remacemide (Admans 2000), and the disordered structure of tetraferrocenyl-[3]-cumulene (Dinnibier *et al.* 2000).

The ease of access to good laboratory diffractometers, however, has encouraged an even greater effort with laboratory data. Structures of high complexity have been solved (e.g.  $\beta$ -Ba<sub>3</sub>AlF<sub>9</sub>, with 29 atoms in the asymmetric unit (Le Bail 1993)), and there has been extensive use of the methodologies in the areas of molecular organic crystals, coordination compounds and organometallic materials (most of the effort in the powder diffraction area has traditionally been in the realm of non-molecular inorganic materials). Eye-catching examples include recent work on bipyridyl complexes of nickel and copper (Masciocchi *et al.* 1996), the carbonyl cluster compound [HgRu(CO)<sub>4</sub>]<sub>4</sub> (Masciocchi *et al.* 1993) and Ph<sub>2</sub>P(O)-(CH<sub>2</sub>)<sub>7</sub>-P(O)Ph<sub>2</sub> (Kariuki *et al.* 1999).

## 2.9 Conclusions

The role of powder diffraction in the structural characterization of materials has expanded dramatically during the last 30 years. A number of developments have played important roles: (a) the advent of the Rietveld refinement method, (b) improvements in laboratory X-ray instrumentation, (c) the availability of

high-resolution powder diffractometers at pulsed neutron sources and synchrotron sources, (d) advances in computational methods for structure solution, and (e) improvements in computer hardware (e.g. personal computers that are capable of running Rietveld codes). The power of powder techniques is such that they have had an impact in most of the major developments in the field of new materials during recent years; solid electrolytes, high-temperature superconductors, fullerenes, zeolites and giant magnetoresistance (GMR) materials are obvious examples. As a consequence, powder diffraction has been transformed from the ugly duckling of crystallography into one of the most exciting and fast-moving areas.

Notwithstanding the remarkable progress, much work remains to be done. The solution of unknown structures from powder data is by no means routine, and the methods need to be further automated before they can be used by non-specialists, even those with crystallographic experience. Furthermore, there is considerable scope for advances in refinement procedures, in spite of the power of the Rietveld method. For example, some of the complex structures that are now being solved are at the limit of what can be refined by current procedures. As a consequence, the accuracy of many of these more complex structures falls well short of what we would hope for and aspire towards. This can easily be seen by looking at the bond lengths that are obtained from refinements of complex organic or zeolitic materials; it is not unusual to find interatomic distances that are clearly outside the range that would be considered to be chemically acceptable.

The solution to this problem will no doubt come from several areas. First, it will become possible to collect better data, and more of it, especially with access to short X-ray wavelengths at the third-generation synchrotron sources (systematic errors in X-ray data can be dramatically reduced at shorter wavelengths). Second, the simultaneous analysis of X-ray and neutron data is already having an impact, but we shall no doubt see the use of data from other techniques such as solid state NMR and EXAFS. In addition, advances in computation are taking us towards a scenario where energy minimization will become a part of the refinement procedure. For example, it is already clear that we can sometimes calculate the structure of an all-silica zeolite with better accuracy than we can determine it experimentally by powder X-ray diffraction (Cheetham *et al.* 1997). Finally, we shall see the use of more subtlety in the refinement process, such as the more extensive use of maximum-entropy methods (Sakata *et al.* 1990, 1993).

This overview would not be complete without reference to the developments in single crystal methods that may have an impact on powder crystallography. The construction of third-generation synchrotron sources has, once again, focused attention on the possibility of collecting X-ray data from micron-size crystals. Progress in this area has not been as rapid as many had expected, but a recent example from the European Synchrotron Radiation Facility (ESRF) in Grenoble (Noble *et al.* 1997) may offer a glimpse of future possibilities in this

area. Certainly, the use of dedicated synchrotron X-ray stations equipped with CCD type detectors (such as Station 9.8 at the Daresbury Synchrotron Radiation Source (SRS)) is transforming expectations of what can be achieved in terms of structure determination from very small crystals. Nor should we forget the power of the electron microscope for interrogating small crystals. There have been several examples (e.g. Vincent *et al.* 1984; Tsuda and Tanaka 1995) of structure refinements by using higher-order Laue zones (HOLZ) from convergent beam electron diffraction patterns, and this area is likely to attract further attention. Nevertheless, the current capabilities and the exciting opportunities for the future can leave us in no doubt that powder diffraction will continue to play a dominant role in this area for the foreseeable future.

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