
CONTRIBUTED PAPERS

THE CONTRIBUTION OF POWDER DIFFRACTION METHODS TO STRUCTURAL CRYSTALLOGRAPHY: RIETVELD AND AB-INITIO TECHNIQUES

NORBERTO MASCIOCCHI

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, via G. Venezian 21, 20133 Milano (Italy)
E-mail: norbert@csmto.mi.cnr.it

The Renaissance of Powder Diffraction

Although the diffraction of X-rays from powders (microcrystalline samples) had been discovered by Max von Laue shortly after his historical experiment on a single-crystal of KCl (which he crushed, on purpose, to verify his fresh hypothesis on the nature of such experiment), the Powder Diffraction (PD) technique has been seldom used as a structural tool; indeed, while some structural hypotheses on simple ionic compounds could be easily verified on the basis of experimental PD data, mostly collected by the pioneering Debye-Scherrer-Hull technique, it became soon very clear that PD traces could be used as fingerprints in qualitative analysis of crystalline materials of different origins.

For this reason, for more than 50 years PD became a widespread analytical method for the characterisation of soils, ores, rocks, metals, alloys, and, more recently, ceramics, drugs, plastics, dyes and other commodities. The experimental methods have followed up this evolution, by allowing high resolution patterns to be recorded, with better signal-to-noise ratios, simple(r) diffraction geometries and useful attachments, such as high- or low-temperature chambers. This was the time when the Bragg-Brentano-Parrish diffractometers were developed, together with more exotic ones (Guinier, Transmission, Seeman-Bohlin, etc.), which were later improved by better optics, β -filters, monochromators and detectors. Meanwhile, a large number (several thousands) of reliable diffraction data had been collected, and published, as early as 1957, as ASTM or JCPDS-PDF cards, for easy qualitative analysis, using manual searches based on the Hanawalt or Fink methods [1].

However, until the early 80's, most powder diffractometers around the world were not automated, and supplied only chart recordings of the diffraction patterns; many instrument did not have step scanning motors nor high intensity (> 1.0 kW) sources. This meant that, for a long time, qualitative, and, later, semiquantitative, analyses were slow, tedious, but, after some practising, quite reliable. On the very same line, it must be mentioned here that PD became soon a very important tool in forensic [2] science and patent claims, where little uncertainties must be excluded.

It was not until the development of high intensity sources (2-3 kW generators, rotating anodes and, lately, synchrotrons), better optics (with cheap monochromators) and computerised systems allowing both diffractometer control and acquisition of digitised data which could be stored for further use, that PD methods experienced a 'new age', the Renaissance, which pushed several groups around the world to develop suitable software and numerical algorithms, capable to retrieve, out of a diffraction pattern of a complex crystal phase (or of a mixture of phases) as much information as possible. It was therefore recognised that, if suitable hardware and numerical techniques were devised, disentangling the three-dimensional crystal structure from the one-dimensional projection of its reciprocal lattice (the PD diagram), was within reach. This approach has been pioneered by H. M. Rietveld, back in the later 60's [3], for neutron diffraction data, and adapted to conventional X-ray data by Young and co-workers in 1977 [4].

The Rietveld Method

The Rietveld method is based on the assumption that the measured diffraction pattern, normally given as Intensity vs. Scattering Angle 2θ , can be approximated by an analytical expression, containing instrumental and structural parameters; the equations reported below follow the formalism adopted by R. A. Young in his recent book on the subject (1993, IUCR and Oxford University Press, *vide infra*).

For a single phase specimen:

$$y_{ci} = s \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) O_k A + y_{bi}$$

where, for each *i*th point (*i*=1 to, typically, a few thousands, for step-scans of $\Delta 2\theta = 0.02-0.05^\circ$):

s is the scale factor (which depends, inter alia, on the amount of specimen irradiated by X-rays, on their intensity, on the optics used and on the quantum efficiency of the detector);

K represents the hkl triplet (Miller indices) for a Bragg reflection;

L_K contains the Lorentz, polarisation (trigonometric) factors and a (symmetry dependent) multiplicity term.

ϕ is the reflection profile function (normally supplied in its analytical form, such as Gaussian, Cauchy (or Lorentzian), or as their combination, in the Voigt, pseudo-Voigt or Pearson VII formalisms).

O_K is a preferred orientation term which accounts for non-ideal (i.e., non-random) distribution of the crystalline orientations, leading to systematic enhancing of the peak intensities of a certain class of reflections (the so called pole); when studying slabs or surfaces of metals or rocks, this effect is often referred to as texture.

A is an absorption factor [which depends on the thickness of the sample, on the diffraction geometry and on the actual weighted average (air/crystals) linear absorption coefficient, μ] In the most convenient diffraction set-up, the Bragg-Brentano-Parrish mode with infinitely thick sample (1 mm or less, depending on the μ value), *A* is constant throughout the pattern, and is normally included in the scale factor.

F_K is the structure factor for the *K*th Bragg reflection, usually taken as:

$$F_K = \sum_j N_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \exp[-B_j \sin^2 \theta / \lambda^2]$$

where:

h, *k* and *l* are the indices of the *K*th reflection;

x_j , y_j and z_j are the fractional atomic coordinates of the *j*th atom in the model;

N_j is a site occupancy multiplier (accounting either for atoms in special positions, atomic disorder, or both);

f_j is the atomic form factor (corrected for real and imaginary terms) of the *j*th atom;

B_j is, in the isotropic approximation, the atomic displacement parameter (a.d.p., in \AA^2) of the *j*th atom (anisotropic or higher rank a.d.p.'s are rarely used in PD methods).

Y_{bi} is a background value for the *i*th data point.

If one calculates the quantity $S = \sum_i w_i (y_{oi} - y_{ci})^2$, a quantitative estimate of the matching between observed and calculated data is obtained.

w_i is normally taken as $1/y_{oi}$;

Y_{oi} = observed (raw) intensity for the *i*th data point;

Y_{ci} = calculated intensity for the *i*th data point.

Since the *S* value heavily depends on the actual estimates of several (instrumental and structural) parameters [represented by the vector $\mathbf{P} = \{p_1, p_2, \dots, p_n\}$], a minimisation routine is normally applied in order to calculate, through several non-linear least-squares cycles, the best set of parameters [the vector $\mathbf{P}' = \{p'_1, p'_2, \dots, p'_n\}$] i.e. that making the *S* quantity as low as possible. This means, in turn, that the Rietveld method, being nothing else than a complex minimisation procedure, cannot be taken as an active tool, since it can only slightly modify a preconceived model built upon external knowledge. Hence, the Rietveld method is likely to refine the \mathbf{P} vector to \mathbf{P}' one, but does not add information which was not originally supplied. However, it is true that visual inspection of the matching between observed and calculated patterns, more than any numerical quantity derived therefrom, can help in assigning new refinable parameters, leading to a better fit once they are introduced in the model.

But what is the explicit nature of such parameters? Simple examples are hereafter given, with such refinable values in bold face:

$$y_{bi} = \sum_l \mathbf{b}_l (2\theta_i)^l \quad \text{[Power series of } 2\theta_i]$$

$$S \quad \text{[Scale Factor]}$$

$$\phi(2\theta_i - 2\theta_k) = \exp\left[-4 \ln 2 \left((2\theta_i - 2\theta_k)^2 / \mathbf{H}_k^2 \right)\right]$$

[Gaussian Profile about $2\theta_k$]

$$\mathbf{H}_k^2 = U \tan^2 \theta + \mathbf{V} \tan \theta + \mathbf{W}$$

[Angular Dependence of Profile Width]

$$2\theta_k = 2\theta_o - \mathbf{S}_d \cos \theta + f(\mathbf{a}, \mathbf{b}, \mathbf{c}, \alpha, \beta, \gamma)$$

[Zero Angle, Specimen Displacement]

$$\mathbf{a}, \mathbf{b}, \mathbf{c}, \alpha, \beta, \gamma \quad \text{[Lattice Constants]}$$

$$\mathbf{x}_j, \mathbf{y}_j, \mathbf{z}_j, \mathbf{B}_j, \mathbf{N}_j \quad \text{[Atomic Coordinates, B's and Occupancies]}$$

$$O_k = \left(\mathbf{G}_1^2 \cos^2 \alpha + (1/\mathbf{G}_1)^2 \sin^2 \alpha \right)^{-3/2}$$

[Dollase formula for Preferred Orientation]

... and more...

As a consequence, a simple inorganic compound crystallising in the orthorhombic system with, say, **five** independent atoms may require, in order to attain a decent fit, about **30** refinable parameters, which means, in turn, that one must ensure to hit the true minimum of *S* in a 31-dimensional hyperspace. At this stage, i) the starting parameters must be reasonably close enough to the final values; ii) convergence must be achieved very slowly, for example by introducing damping factors; iii) the sequence into which the different parameters are being refined needs to be carefully studied (a few rules of thumb can be found in the literature, but it's one's personal experience on his particular class of samples which drives to the final model ...) and iv) the sagacious introduction of chemically sound constraints (by adding observational equations in the least squares routines) may reduce the conformational space to be spanned.

The quality of the Rietveld refinement fit (ie. the quantitative measure of the matching between observations and the calculated pattern), which *should* afford information about the true values of all parameters in our model (for which an estimated standard deviation, in the least-squares sense, is supplied), is normally evaluated by agreement factors, defined as:

$$R_p = \sum_i |y_{oi} - y_{ci}| / \sum_i |y_{oi}| \quad [\text{R-profile}]$$

$$R_{wp} = \sum_i w_i (y_{oi} - y_{ci})^2 / \sum_i w_i (y_{oi})^2 \quad [\text{Weighted R-profile}]$$

$$R_B = \sum_K |I_{oK} - I_{cK}| / \sum_K |I_{oK}| \quad [\text{R-Bragg}]$$

$$R_F = \sum_K |I_{oK}^{1/2} - I_{cK}^{1/2}| / \sum_K |I_{oK}^{1/2}| \quad [\text{R-F}]$$

where *i* runs over all data points, and *K* runs over all (space-group permitted) reflections. Since *I*_{oK} (observed integrated intensities) are not readily available, a number of numerical algorithms, partitioning the observed intensities of overlapping peaks into their partial contributions have been developed, but will not be discussed here.

When does the Rietveld Method give reliable answers?

From the above considerations, it is obvious that the Rietveld method requires digitised data (i.e., it *cannot*

be used on analogic chart recordings or traces) and knowledge of an approximate structural model (ie., lattice parameters, space group symmetry and fractional atomic coordinates). A number of other starting parameters, mostly instrumental, can be guessed by visual inspection (background coefficients, zero angle, etc.) or refined to reasonable values from arbitrary choices (this is particularly true for the scale factor, which can be determined by linear least-squares in a single cycle at the very beginning of the simulation).

The most simple application of the Rietveld method, which acts also as a benchmark for beginners, is the attempt to refine a simple standard monophasic sample, for which all structural parameters can be taken as granted from the literature. Typically, well crystallised powders of silicon, tungsten, KCl, NaCl, or, more recently, LaB₆, have been used; many of them have atoms lying in special positions, so that there is no freedom in refining their locations. When analysing such simple data, one must ensure that all instrumental parameters which affect the whole pattern have been tested and, eventually, refined. They include, if sample preparation did not afford a randomly oriented powder specimen, the choice of the *O*_K pole and the refinement of the preferred orientation parameter. Therefore, the final output of the Rietveld refinement will contain a number of refined parameters which are, *all together*, indicative of the quality of the pattern, and, more important, of the resolution of the instrument, together with hints on the proper alignment of optics and sample axis. For example, if the zero angle error is found to exceed 0.02° (2θ), realignment of the instrument might be useful...

Of course, the Rietveld technique has been used for the structural characterisation of many materials, ranging from simple inorganics and minerals, to macromolecular (polymer) chemistry, with *ad hoc* modification of the methodology and instruments.

The most reliable values which can be obtained by a standard Rietveld approach are probably the lattice parameters, since they are less biased by errors in the structural model. Indeed, since the peak positions can easily be determined even without reference to the real structure, some modification of the original Rietveld method have been proposed, which refine directly integrated intensity values (i.e. |F|²), without

any reference to a structural model. These methods, pioneered by Pawley in 1981 [5], have been later developed, using a number of different mathematical tricks to ensure least-squares stability, by Toraya [6], Will [7], Le Bail [8] and, recently, Giacobozzo's groups [9]. They become nowadays very important in the structure solution process, later discussed in the Ab-initio chapter. However, if a series of compounds have been treated under slightly different circumstances (such as thermal, pressure or composition gradients), curves representing the variation of the lattice parameters (and cell volumes) vs. the physically important thermodynamical parameter (T , P , χ) can easily afford thermal expansion coefficients, dV/dP parameters, and solid solution behaviour, which might, all together, lead to the construction of a complete phase diagram for the species under study.

On the other hand, if a structural model of an isomorphous or isostructural compound is known, the Rietveld refinement can easily afford the correct atom locations in the unit cell, which, together with the refined lattice parameters, allows interpretation of the whole structure in terms of bond distances, angles and torsions (to be compared with the archetypal model). For example, a detailed comparison among similar structures can reveal subtle ionic-covalent effects or information about the valence state of the ions in inorganic matrix. A warning is however here necessary: since the fractional atomic coordinates are much more in error than lattice parameters and despite their associated e.s.d.'s seems to suggest a high precision, I personally doubt that, particularly for light(er) atoms, one should rely on such values, unless the experiment has been done with special care and the structure contains only a few (four or less) independent atoms. In this context, it is customarily assumed that, when the complexity of the structure is higher (as in zeolites or in low symmetry systems), the introduction of 'soft' constraints (which, by the way, can bias the refinement by imposing external, *a priori*, prejudice) may improve the overall knowledge of the sample under study. On the very same line, the interpretation of site occupancy and B values might be somewhat difficult, since they correlate very much also with instrumental, i.e. non structural, parameters, such as background evaluation, sample illumination and transparency and preferred orientation parameters.

However, the Rietveld technique may be used in a number of other fields, giving mostly information on the molecular shape, conformation and crystal packing. When the complexity of the structural problem is too high (and only conventional X-ray radiation and equipment are used), the independent atoms model may not lead to chemically significant values for all geometrical features; this is the case for molecular compounds (for which, *inter alia*, the high angle portion of the powder pattern contains little information, because of large thermal displacements and overlapping of several hundreds of reflections), being even more dramatic for polymeric (organic or metallorganic) compounds of low crystallinity. In both cases, it has been found that a slightly different approach might be used: the structure factors are computed on the basis of *actual* fractional atomic coordinates, but the refinable parameters, i.e. those for which the least-squares matrix contains first (and second) derivatives of S , are now internal geometrical parameters, which can easily be constrained to be equal to each other within chemically similar environments without adding new observational equations [10]. This method has originally been used for simple organic polymers (possessing very broad peaks and poorly resolved diffraction patterns) and has been lately used for complex molecular systems. It is possible that the future directions of numerical treatment of Rietveld analysis will afford better numerical techniques capable to tackle these classes of compounds in a more reliable manner. It should be emphasised here that coupling different observations on the same specimen (X-ray and neutron diffraction), spectroscopic (NMR, EXAFS, IR) information and packing energy computations in the periodically updated crystal lattice (once a proper force field has been developed), might afford results which are of higher quality than those obtainable by a single method (such approach, however, requires a more careful analysis of all systematic errors and of model building than it is normally done.).

Quantitative Analysis by the Rietveld Method

Since the general mathematical formula of the integrated intensity (of the i th peak) scattered by a monophasic specimen (a phase) in the Bragg-Brentano-Parrish mode can be represented as follows:

$$I_{ii} = I_o \lambda^3 / 64\pi R \cos^2 \theta_m / \mu \left(e^2 / mc^2 \right) M V_{\alpha}^2 |F_{ii}|^2 \\ \times \left\{ (1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta) \right\} \text{ (Young, 1993)}$$

it can be shown that, for a phase α contained in a mixture of amorphous or polycrystalline materials the above formula can be best rewritten as: $I_{ii} = K_e K_{i\alpha} / \mu$ (K_e is an instrumental, geometrical and experimental factor, independent on the phase α , $K_{i\alpha}$ contains the structural information, such as structure factor, multiplicity, lattice volume, etc., for the phase α); for a mixture of several crystal phases,

$$I_{ii} = K_e K_{i\alpha} \chi_{\alpha} / [\rho(\mu/\rho)_m] \quad [\text{eq. A}]$$

where χ_{α} is the molar fraction of the α phase.

$(\mu/\rho)_m = \sum_p \chi_p (\mu/\rho)_p$ is the weighted average μ/ρ value. This holds for all (α, β, ω) phases in the mixture.

In the Rietveld notation,

$$y_{ci} = s \sum_K K_{i\alpha} \phi(\Delta 2\theta_{iK,\alpha}) + y_{bi}, \text{ for one crystal phase} \\ y_{ci} = \sum_p s_p \sum_K K_{in} \phi(\Delta 2\theta_{iK,p}) + y_b, \text{ for N crystal phases.} \quad [\text{eq. B}]$$

On combining equations [A] and [B], one gets:

$$s_{\alpha} = K_e \chi_{\alpha} / [\rho_{\alpha}(\mu/\rho)_m] \text{ or, explicating } \chi_{\alpha}: \\ \chi_{\alpha} = s_{\alpha} \rho_{\alpha} (\mu/\rho)_m K_e \quad [\text{eq. C}]$$

Under the assumption that all phases are crystalline (and known), one can estimate the phase fraction simply by imposing, in the absence of amorphous phases,

$$\sum_p \chi_p = 1, \text{ i.e. } \chi_p = \chi_p / (\chi_{\alpha} + \chi_{\beta} + \dots \chi_{\omega}) \quad [\text{eq. D}]$$

On combining equations [C]+[D], one gets $\chi_p = s_p \rho_p / \sum_K s_K \rho_K$, which is the basic formula for quantitative analysis using the Rietveld method. Note, however, that different programs include different variables in $K_{i\alpha}$, so one should always check the current definition of s_p ; for example:

$$s_p = S_{\text{GSAS}} V_p \text{ in GSAS [11], and}$$

$$s_p = S_{\text{DBW}} V_p^2 \text{ in DBW [12]}$$

Therefore, if allowance for a multiphase system is made in a Rietveld program, one may obtain, from the experimentally determined scale factors, a quantitative estimate of the phase contents. This method is, at present, the most reliable quantitative assessment which can be obtained from XRPD data; however, other single-peak/multiple-peaks methods have been developed in the past, and are still in use [13].

More than ever, the sample preparation must be carefully performed, since uneven sampling or texture effects might afford rather different values; the expected uncertainties for quantitative analyses based on the Rietveld methods are estimated in a few molar percent (or less) therefore, it is very critical to measure accurately the phase fraction of materials which are present below the 5% level. Recently, this method has been slightly modified in order to assess the phase fraction of each component (and of the amorphous content) in a general case, with the addition of weighed amounts of external standards [14].

Ab-initio Structure Solution from Powder Diffraction Data

Since the concept of molecular structure plays a central role in chemistry, much work has been done to structurally characterise as many molecules as possible. Surely single crystal X-ray diffraction is the easiest, quickest and most definitive method applied. However, there are many compounds which, for different reasons, do not afford single crystals of suitable size and quality. It would be unfortunate if the structure of a class of molecules, or even that of an individual compound, were ignored, simply because single crystals could not be easily obtained.

With the improvement of the experimental and numerical techniques now available, the determination of crystal structures from powder diffraction data has recently become a viable tool for assessing a number of structures which could not be solved by more conventional (i.e. single-crystal) methods. However, the procedure which eventually leads to the correct structural model is by no means simple, and requires a lot of efforts, which have no real counterpart in the single-crystal technique. For example, while it is well known that poor single-crystal diffraction data can still afford gross molecular features which are often enough from an analytical point of view, the use of less than perfect powder diffraction data may lead nowhere, hampering, for example, the very basic

procedures of finding the lattice constants (indexing) or phasing of the reflections.

Therefore, it is highly recommended that structure solution (not merely structural refinement) from powder diffraction data should be undertaken only if suitable single crystals cannot be grown, even after through and repeated attempts of crystallisation. This means, in turns, that there are classes of compounds which will be undoubtedly benefit of his new methodology, since they do not appear as single crystals:

i) Compounds which cannot be recrystallised: insoluble species, which cannot be dissolved in normal (organic) solvents; thermally unstable compounds, which cannot be recrystallized from their melt [15].

ii) Twinned crystals, particularly those which show Twin Quasi-Lattice Symmetry, for which sampling of the scattered intensity on a 4-circle diffractometer is either impractical or impossible [16]. [The powder diffraction method, by definition, integrates over all orientations of the reciprocal space, and therefore, is blind to the presence of (macro)twins, since they are treated as independent particles of the whole collection; however, if the size of the domains becomes nanoscopic, (microtwinning), both single-crystal and PD techniques will result in disordered structures. However, in this case, owing to the complete sampling of the reciprocal space, PD, through the analysis of the asymmetry of the peak shapes, might be able to suggest the correct twinning model].

iii) Metastable phases, which, upon recrystallisation or further manipulation, generate a different species, or, maybe, polymorphs. This can happen upon irradiation (for photochemically induced transformations [17]) or exposure to electric or magnetic fields (inducing, for example, magnetic ordering detectable by neutron diffraction). Metastable polymorphs [18] exist on kinetic grounds only, and may not be restored upon manipulation.

iv) Products of solid/gas, solid/liquid or solid state reactions: on reacting a solid crystalline material with other species, it is unlikely that the crystal integrity is maintained. Only a few cases are known which show retention of the single crystal features, and typically refer either to gas/liquid permeation in porous media or topotactical rearrangements in molecular crystals. Most single crystals are fragmented in such condi-

tions, some generating amorphous species, but seldom microcrystalline powder products can be found [19].

The complexity of the structures which can be solved at atomic resolution by single crystal analysis (thus forgetting protein crystallography) reaches, nowadays, a few hundreds independent atoms. Differently, PD is likely to afford a decent stereochemical picture for sample containing not more than 10-15 atoms in the asymmetric unit. A few reports of higher complexity are found in the literature, but require external knowledge and stereochemical hypotheses. Therefore, only a limited number of structures can be successfully studied by PD methods. Moreover, there is still a gap between the complexity which could be tackled in the refinement procedure by the Rietveld method, and that which is likely to be solved by *ab-initio* studies.

The process of crystal structure solution from PD data is still in its infancy [20], and not at all well described and linear, since rethinking of all previously taken decisions (at any step) is the rule, not the exception. In the following, a few steps are indicated, with some tricks deriving from personal experience, but more might be necessary in order to build, complete and refine the final model.

a) Data collection: since the first step (often the most difficult and always the limiting one) of a structure solution from PD data is the determination of the unit cell parameters (requiring accurate peak positions, rather than reliable peak intensities), as a general strategy, two distinct data collection procedures can be performed: one for indexing, where a thin sample deposited on a quartz monocrystal (zero-background sample holder, obtainable from *The Gem Dugout*, State College, PA) with the aid of a binder (5% collodion in amyl acetate), with the narrowest slits available, thus minimising various systematic errors (sample transparency, axial divergence, etc.); the second, for structure solution and refinement, since it is imperative to measure peak intensities as accurate as possible (the most serious problems arising from particle statistics and preferred orientation effects); data should be collected, on a sample prepared by the side-loading technique, with longer counting times (such as 10s) and different (wider) optics.

b) Standard peak search methods, possibly improved by α_2 stripping, smoothing and profile fitting, can afford a limited (typically <20) number of peak locations of more or less resolved low angle lines.

c) Indexing is usually one of the most difficult steps to be performed. There are a number of different programs and algorithms which can, and must, be jointly used in order to increase the chances of success; it is likely that they will afford several possibilities, which, in absence of a structural model, are all more or less equiprobable, on numerical grounds only. Since "the ultimate check for the correctness of any lattice metric based on powder diffraction data is the satisfactory refinement of the structure [21]", one takes a ranking procedure and may choose the probable, but not necessarily true, unit cell parameters. At this stage the use of empirical relations [22] and external knowledge can undoubtedly help in assigning, and recognising, out of a bunch of several lattice metrics with similar figures of merit, the correct values.

d) At this stage, the individual structure factor moduli can be obtained by a whole-pattern profile fitting technique, in which the observed pattern is matched by a calculated one, obtained by varying the intensities of the space-group allowed reflections (*if known*), together with the standard instrumental and lattice parameters, by least-squares [6, 7] or other (more stable) methods [5, 8, 9]. Pattern decomposition is usually performed in largest 2θ range, depending on the pattern complexity; however, above 60 or $70^\circ 2\theta$, a featureless trace is often observed and the fit becomes merely numerical, without physical significance; therefore, the more reliable intensities extracted by this procedure are those at low angle section, which contains reflections less affected by accidental overlap.

e) A number of structural tools have been developed for solving the phase problem: most structures were, and are, solved by two very different but powerful techniques: Patterson synthesis, and Direct methods; other methods employed in this field are Real space scavengers [23], Monte Carlo methods [24], Maximum Entropy and Likelihood methods [25], TEM imaging [26], Database retrieval, Geometrical modelling, etc.; all these latter methods can be used, at least in principle, also for single-crystal data, but, owing to the high success rate of Patterson and Direct methods in the single crystal case, have been origin-

ally developed in order to tackle the complexity of the structure solution process from PD data. In addition, it has been found that Patterson maps from PD data are likely to afford approximate metal atom locations even in the presence of complex organic ligands, if only a small portion of data (the low-angle, i.e. the most intense ones) is available [18]. Differently, Direct Methods, being based upon statistical assumptions, may need a larger set of accurate data, which may not be always available. At this stage, given that difference Fourier maps calculated from powder diffraction data are more diffuse than those calculated from single crystal ones and are also biased towards the partial model which is used in the partitioning of the observed intensities for overlapping reflections, a few tricks may help in completing the correct structural model: i) as the information on the missing (light) atoms are essentially contained in the low angle data, while at high angles the pattern is much more sensitive to the metal atom locations, one should perform the refinement of the partial model against high angle data only (say, $>40^\circ$), obtaining either more accurate coordinates and the proper scale factor, which can later be used for the whole pattern simulation, thus affording a more interpretable difference Fourier map; ii) as the knowledge of the stereochemistry of stiff ligands and crystal packing considerations can be used for judging the adequacy of Fourier peaks and also for finding missing atoms, an accurate geometrical modelling, within the crystal lattice (checking intermolecular contacts between atoms) can be performed; such computations typically allow to discard a number of otherwise plausible conformations.

f) Final Rietveld Refinement: since the stability of Rietveld least-squares refinements is of limited power, strictly depending on the number of 'effective' observations (which is much lower than the total theoretical reflections convoluted in the whole pattern) a number of geometrical soft constraints is normally required. Moreover, the low angle data (say, with $2\theta < 18^\circ$), most affected by instrumental aberrations (sample illumination, axial divergence, etc.) need to be omitted in the final cycles. In addition, since e.s.d.'s for the light atoms are biased by the introduction of soft constraints and their relative weights, more statistically sound values can be obtained after a last cycle of refinement with the weight of the soft constraints set to zero. Summarising, while from PD data many details of the

molecular structure parameters cannot be evidenced, nevertheless, valuable (otherwise inaccessible) crystallochemical information, such as stoichiometry, shape and conformation of the molecules under study, can be retrieved.

Some Interesting Places for Further Readings

- H. R Klug and L. E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley-Interscience, New York, **1974**.
- *Modern Powder Diffraction*, D. L. Bish and J. E. Post Eds., *Reviews in Mineralogy*, vol. 20, The Mineralogical Society of America, Washington, D.C., **1989**.
- *The Rietveld Method*, R. A. Young Ed., International Union of Crystallography, Oxford University Press, **1993**.
- *The Contribution of Powder Diffraction to Structural Crystallography. Rietveld and Ab-initio Techniques*, Ricerca Scientifica ed Educazione Permanente, Supp. 98, **1995**, University of Milano.
- D. K. Smith and S. Gortner, *Powder Diffraction Program Information 1990 Program List*, *J. Appl. Crystallogr.*, **1991**, 24, 369.
- J. I. Langford and D. Louër, *Rep. Prog. Phys.*, **1996**, 59, 131.

References

[1] Powder Diffraction File, ICDD, International Centre for Diffraction Data, Newtown Square, PA.

[2] P. J. Thatcher and G. P. Briner, *Powder Diffr.*, **1986**, 1, 320.

[3] H. M. Rietveld, *Acta Crystallogr.*, **1967**, 22, 151; H. M. Rietveld, *J. Appl. Crystallogr.*, **1969**, 2, 65.

[4] R. A. Young, P. E. Mackie and R. B. Von Dreele, *J. Appl. Crystallogr.*, **1977**, 10, 262; R. A. Young and D. B. Wiles, *J. Appl. Crystallogr.*, **1982**, 15, 430.

[5] G. S. Pawley, *J. Appl. Crystallogr.*, **1981**, 14, 357.

[6] H. Toraya, *J. Appl. Crystallogr.*, **1986**, 19, 440.

[7] E. Jansen, W. Schäfer and G. Will, *J. Appl. Crystallogr.*, **1988**, 21, 228.

[8] A. LeBail, H. Duroy and J. L. Fourquet, *Mat. Res. Bull.*, **1988**, 23, 447.

[9] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Buria, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, **1994**, 27, 435.

[10] S. Bruckner and A. Immirzi, *J. Appl. Crystallogr.*, **1997**, 30, 207.

[11] A. C. Larson and R. B. Von Dreele, LANSCE, MS-HBO51 Los Alamos National Laboratory, NM, **1990**.

[12] A. Sakthivel and R. A. Young, DBWS-9006PC, Georgia Institute of Technology, Atlanta, GA, **1990**.

[13] R. L. Snyder and D. L. Bish, *Quantitative Analysis, in Modern Powder Diffraction*, D. L. Bish and J. E. Post, Eds, **1989**.

[14] A. Gualtieri, *Powder Diffr.*, **1996**, 11, 97.

[15] N. Masciocchi, M. Moret, P. Cairati, F. Ragaini and A. Sironi, *J. Chem. Soc., Dalton Trans.*, **1993**, 41; N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia, and G. La Monica, *J. Amer. Chem. Soc.*, **1994**, 116, 7768.

[16] J. Li, F. Mc Culley, S. L. McDonnell, N. Masciocchi, D. M. Proserpio and A. Sironi, *Inorg. Chem.*, **1993**, 32, 4829.

[17] N. Masciocchi, A. Kolyshev, V. Dulepov, E. Boldyreva and A. Sironi, *Inorg. Chem.*, **1994**, 33, 2579.

[18] N. Masciocchi, G. A. Ardizzoia, G. La Monica, M. Moret and A. Sironi, *Inorg. Chem.*, **1997**, 36, 449.

[19] N. Masciocchi, M. Moret, A. Sironi, G. A. Ardizzoia, S. Cenini and G. La Monica, *J. Chem. Soc., Chem. Commun.*, **1996**, 1351.

[20] K. D. M. Harris and M. Tremayne, *Chem. Mater.*, **1996**, 8, 2554.

[21] P. E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, **1985**, 18, 367.

[22] G. S. Smith, *J. Appl. Crystallogr.*, 1976, 9, 424; G. S. Smith, *J. Appl. Crystallogr.*, **1977**, 10, 252; C. J. E. Kempster and H. Lipson, *Acta Crystallogr.*, **1972**, B28, 3674.

[23] N. Masciocchi, R. Bianchi, R. Cairati, G. Mezza, T. Pilati and A. Sironi, *J. Appl. Crystallogr.*, **1994**, 27, 426.

[24] K. D. M. Harris, M. Tremayne, P. Lightfoot and P. G. Bruce, *J. Am. Chem. Soc.*, **1994**, 116, 3543.

[25] M. Tremayne, P. Lightfoot, M. A. Mehta, R. G. Bruce, K. D. M. Harris, K. Shankland, C. J. Gilmore and G. Bricogne, *J. Solid State Chem.*, **1992**, 100, 191.

[26] Y. A. Barbanenkov, N. D. Zakharov, I. R. Zibrov, V. R. Filonenko, P. Werner, I. Popov and M. D. Valkovskii, *Acta Crystallogr.*, **1993**, B49, 169.

