

Crystal Structure of Non-molecular Compounds from Powder Diffraction

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Methods of structure determination from powder diffraction of non-molecular compounds (inorganics, extended solids, intermetallic compounds, *etc.*) are reviewed. They work either in reciprocal space or in direct space. Those working in reciprocal space use algorithms known from single crystal works (direct methods and Patterson synthesis) and need decomposition of powder patterns to individual reflections. Those working in direct space need no powder pattern decomposition and are based on global optimization of a structural model to improve agreement between the observed and calculated diffraction patterns. The available computer programs working in direct space are summarized.

INTRODUCTION: WHY ARE POWDERS MORE DIFFICULT THAN SINGLE CRYSTALS?

Powder diffraction using X-rays and neutrons plays a major role in the search for new materials that are not available in the form of single crystals. Moreover, most of the industrial applications of inorganic and organic compounds are in the form of polycrystalline materials (*e.g.*, metal hydrides for storage and battery applications, metallic and intermetallic compounds in industry, thin films, organic compounds in pharmaceutical industry, *etc.*). Structure determination from powder diffraction (SDPD) is more difficult than structure determination on single crystals, because the available data are a projection of a three-dimensional diffraction pattern onto one dimension (radial distance from the reciprocal space origin), and consequently the diffraction peaks are overlapped. Extraction of structure factor amplitudes can be further complicated by a broadening (often anisotropic) due to the crystal lattice defects. There are two alternative solutions to this problem when trying to solve a crystal structure from

powder data: either we try to improve the decomposition of the observed powder pattern into individual peaks, or we try to model the observed pattern as a whole.

In this paper, we review both methods as applied to compounds that do not contain isolated molecules (extended solids), *i.e.*, most inorganic compounds. Molecular compounds like organics, or hybrids like coordination compounds, are in principle treated by the same approach. However, here we do not review the description of molecules by internal coordinates, use of knowledge of molecule conformation obtained by other methods, active use of organic structure databases and energy minimization of molecular crystals.

DECOMPOSITION OF OVERLAPPING REFLECTIONS

Decomposition of overlapping reflections in a powder pattern is done according to the Rietveld method,¹ *i.e.*, treating each point in a digitized powder pattern as an independent observation. The only difference compared

to the Rietveld refinement is the treatment of integrated intensities: in the Rietveld refinement they are calculated from the actual structural model, in the pattern decomposition they are treated as free parameters. Two actually used alternatives of their treatment are the Pawley type of fitting² and the Le Bail iterative method.³ In the Pawley method, integrated intensities are fitted by the optimization algorithm (usually least-squares based) like any other free parameter (lattice, profile parameters, background, *etc.*). Consequently, the method suffers from non-realistic resulting values (negative) of strongly correlated integrated intensities. The problem was solved either by applying the Bayesian probability approach⁴ or by active use of the variance-covariance matrix resulting from the Pawley fit in a structure solution procedure.⁵ Le Bail method is based on the iterative use of the Rietveld decomposition formula, originally used by Rietveld for obtaining the values of "observed" integrated intensities at the end of the Rietveld refinement.

Powder pattern decomposition can be further improved by the active use of additional information extracted from the pattern or by several independent observations of diffraction data.

Use of Additional Crystallographic Information

In the program EXPO⁶ for SDPD, different crystallographic information is used to improve the pattern decomposition:

(i) Pseudotranslation symmetry is used with the basic idea: When a super-structure reflection overlaps with a sub-structure reflection, it is more probable that the second one is stronger.

(ii) Positivity of the Patterson function: Patterson function is calculated from non-overlapped reflections, and then non-linearly modified and forced positive. From this modified Patterson function, we can get all structure factors moduli by back transformation.

(iii) Phasing information from already located partial structure (molecular fragment).

In the DOREES-POWSIM program,⁷ besides the active use of the Patterson function positivity, the triplet relation

$$|Eh| \approx \sum_k |Ek| |E-h-k|$$

allows to conclude from the knowledge of two members $|Ek|$ and $|E-h-k|$ of a strong triplet that the third member $|Eh|$ is probably also strong.

Modification of the Patterson map was actively used in the powder pattern decomposition either by applying the maximum entropy approach⁸ or using Sayre's argument "Second power of a Fourier map is similar to the Fourier map itself" applied iteratively as Fast-Iterative-Patterson-Squaring – FIPS.⁹

Use of Several Diffraction Patterns

Several powder patterns measured at different but controlled external conditions, which vary the intensities in a known way, can provide information on the intensities of overlapping reflections. Two external parameters were successfully applied:

(i) Temperature as anisotropy of thermal dilatation, first proposed by Zachariasen and Ellinger,¹⁰ and

(ii) Texture as anisotropy of the orientation distribution function of crystallites.¹¹

Anisotropy of Thermal Dilatation. – A compound with anisotropic thermal dilatation will show, in powder diffraction patterns measured at sufficiently different temperatures, the "anisotropy" of peaks overlapping, *i.e.*, reflections overlapped at one temperature will be well separated at another temperature and *vice-versa*. The theory of this method based on the Bayesian probability approach was described and a practical example was given.¹² The most complex structure solved by using the data decomposed by this method can be found in Brunelli *et al.*¹³ (48 non-hydrogen atoms in the asymmetric unit, four independent molecules).

Texture. – The idea of this method is again very simple and seems to be very powerful, because the texture is an external effect that changes the integrated intensities of reflections in very anisotropic, but easily understandable manner, and the changes can be as important as by several orders of magnitude. Several groups have tried to exploit the practical application of the method. The most developed methodology can be found in Baerlocher *et al.*,¹⁴ who used the most general description of the texture by the orientation distribution function. Simplifications by using empirical texture functions, like a simple Gaussian (known as the Rietveld texture correction) or March-Dollase function proposed by Černý,¹⁵ were shown to have a limited range of applicability. The most difficult problem of this method seems to be the preparation of a sample with a strong texture, which is important for a good resolution of the method. The principle of the method can be easily understood as a system of m equations for n unknowns:

$$I_{\text{tot}}(\alpha_1) = I_1T_1(\alpha_1) + I_2T_2(\alpha_1) + \dots + I_nT_n(\alpha_1)$$

$$I_{\text{tot}}(\alpha_2) = I_1T_1(\alpha_2) + I_2T_2(\alpha_2) + \dots + I_nT_n(\alpha_2)$$

$$\dots \dots \dots m \geq n$$

$$I_{\text{tot}}(\alpha_m) = I_1T_1(\alpha_m) + I_2T_2(\alpha_m) + \dots + I_nT_n(\alpha_m)$$

where I_{tot} is the total measured intensity of a cluster of n overlapped reflections I_i ($i = 1 \dots n$), each having its known texture correction factor T_i determined from several non-overlapping reflections either as the orientation distribution function or as an empirical texture correc-

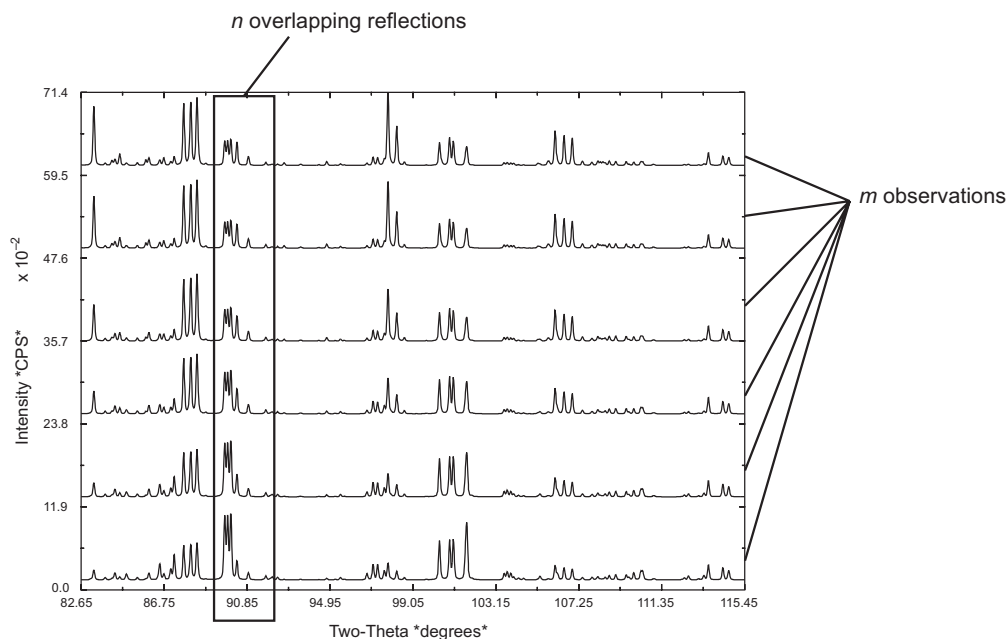


Figure 1. Demonstration of the principle of the texture method of powder pattern decomposition: part of simulated patterns of CrCl_3 from the Bragg-Brentano goniometer with χ -inclination. From top to bottom: $\chi = 0, 15, 30, 45, 60$ and 75 deg (from Černý).¹⁵

tion function. The m diffraction patterns are measured under different conditions, changing the texture effect on integrated intensities, e.g., the inclination angle α_i on a texture goniometer. A demonstration of the method with calculated patterns of CrCl_3 is given¹⁵ in Figure 1.

STRUCTURE SOLUTION

The SDPD methods can be divided into two groups according to the working space, as found in David *et al.*¹⁶ and references therein:

(i) Reciprocal space methods: They use procedures developed for single crystal data, such as direct methods or Patterson synthesis, and optimized for powder data. They need structure factor amplitudes obtained by powder pattern decomposition.

(ii) Direct space methods: Different algorithms for searching in the direct space of structural parameters are used, and the agreement factor between the observed and calculated powder diffraction data is evaluated, and the structural model is optimized to improve the agreement.

Reciprocal Space Methods

Direct methods applied to data obtained by powder diffraction suffer from a lack of precise structure factor amplitudes down to necessary resolution (~ 1 Å for organic compounds, higher for heavy atom compounds) due to the peak overlap. Lower precision of the structure factors amplitudes from powder data is the reason why the standard statistical tests of direct methods (Wilson test, E -distributions, Figures-of-Merit) do not always work

properly. Three direct method programs were optimized for working with data from powder diffraction: EXPO,⁶ DOREES-POWSIM⁷ and XLENS,¹⁷ a program based on the modulus sum function.

Patterson synthesis is a robust method, which works also with low-resolution data; however, the Patterson maps obtained from powder diffraction data suffer from blurring. The problem was treated with image reconstruction based on the maximum entropy approach.⁸ The maximum entropy principle can be applied during the electron density map calculation,¹⁸ but also already in the decomposition of overlapping reflections, as shown in the MICE program¹⁹.

Direct Space Methods

Some Definitions (from A. Le Bail's Talk at ESCA-9, Egypt 2004). – Sometimes the "direct space methods" (not to be confused with the direct methods) are called "global optimization methods" or "model building methods", and sometimes even "real space methods". "Direct space" was the definition use in the pioneering papers. "Direct space" as opposed to "reciprocal space" has an adequate crystallographic structural sense, and should be preferred to "real space", which as opposed to "imaginary", would call to mind both parts of the diffusion factors. "Global optimization" has a broad sense and designates the task of finding the absolutely best set of parameters in order to optimize an objective function, a task not at all limited to crystallography.

Under the name direct space methods we do not mean the interpretation of electron density or Patterson maps by searching for molecular fragments, even if they

TABLE I. List of available computer programs that make use of the direct space method for SDPD

Program	Access ^(a)	GO ^(b)	CF ^(c)	Reference	www
DASH	C	SA	P	David <i>et al.</i> ³⁷	www.ccdc.cam.ac.uk
EAGER	A	GA	WP	Kariuki <i>et al.</i> ³³	www.cardiff.ac.uk/chemy/staff/harris.htm
(former GAPSS)					
ENDEAVOUR	C	SA	I+E	Putz <i>et al.</i> ³⁸	www.crystalimpact.com
ESPOIR	O	MC	L	Le Bail ³⁹	www.cristal.org
FOX	O	SA(PT)	WP,I,AC	Favre-Nicolin and Černý ³⁴	objcryst.sourceforge.net
OCTOPUS	A	MC	WP	Tremayne <i>et al.</i> ⁴⁰	www.cardiff.ac.uk/chemy/staff/harris.html
POSSUM	A	DE	WP	Seaton and Tremayne ⁴¹	www.chem.bham.ac.uk/labs/tremayne
POWDERSOLVE	C	MC	WP	Engel <i>et al.</i> ⁴²	www.accelrys.com
PSSP	O	SA	L		powder.physics.sunysb.edu/programPSSP/pssp.html
SAFE	A	SA	WP+SE	Brenner <i>et al.</i> ⁴³	www.crystal.mat.ethz.ch
SA	A	SA	WP	Andreev <i>et al.</i> ²⁶	ch-www.st-andrews.ac.uk/staff/pgb/group
TOPAS	C	SA	I,WP,E	Coelho ⁴⁴	pws.prserv.net/Alan.Coelho
ZEFSAII	O	MC(B)	I+AC	Falcioni and Deem ²⁷	www.mwdeem.rice.edu/zefsaII
ORGANA	A	MC(E)	I+E	Brodski <i>et al.</i> ⁴⁵	
FOCUS	O		I+TS	Grosse-Kunstleve <i>et al.</i> ⁴⁶	www.crystal.mat.ethz.ch

^(a) C = Commercial at academic prices, O = Open access, A = Contact the authors.

^(b) GO = Global Optimization: MC = Monte Carlo, MC(B) = biased Monte Carlo, MC(E) = Energy guided Monte Carlo, SA = MC+Simulated Annealing, PT = Parallel Tempering, GA = Genetic Algorithm, DE = Differential Evolution.

^(c) CF = CostFunction: P = Pawley, L = Le Bail, I = Integrated intensities, WP = Whole Pattern, E = potential energy, SE = structure envelopes, AC = Atomic Coordination, TS = Topology Search.

work in direct space and use a global optimization algorithm such as the genetic algorithm.²⁰ These methods still need structure amplitudes, *i.e.*, decomposition of a powder pattern, which is avoided by the direct space methods mentioned here.

History. – The first successful attempt to solve a crystal structure by an automatic (not manual!) localization of a building block (rigid molecule) in the direct space can be seen in the RISON program,²¹ which was then modified for powder data as P-RISON.²² The optimization algorithm used was the constrained least-squares refinement, which is limited to structures not bigger than 10 independent atoms and which resulted in only approximate atomic positions.

Pannetier *et al.*²³ were one step from being the first to use a true global optimization algorithm – simulated annealing (SA) for structure solution from powder data. However, they did not believe in the power of the method: "At present the method is not efficient enough for use in most practical problems of *ab-initio* structure determination." The authors used SA for structure prediction based on optimization of the crystal potential energy. Thus, the first use of a global optimization algorithm (SA) in the structure solution from powder data is attributed to Newsam *et al.*²⁴ even if the structure solved in the paper was known and small (benzene). Later on, the direct space method of structure solution from powder data developed rapidly, using different algorithms, like the

Monte Carlo (MC) search²⁵ and genetic algorithm (GA).⁵ An essential step forward was achieved by applying the description of structural blocks by internal coordinates, like bond distances, angles and torsion angles, by Andreev *et al.*,²⁶ thus allowing a direct stereo-chemical interpretation and/or constraining of optimized structural parameters. Modification of SA called parallel tempering algorithm (PT) was first used in the SDPD by Falcioni and Deem.²⁷ Since then, the list of programs dealing with direct space methods of structure solution from powder (but also single crystal) X-ray and/or neutron diffraction data has continued to grow. For a review see Table I and <http://www.cristal.org/> or <http://www.ccp14.ac.uk/>.

Principles. – The flow chart representing a typical implementation (like in the FOX program) of the global optimization approach to the crystal structure solution from powder diffraction data is given in Figure 2. Direct space methods are based on the location of building blocks in the elementary cell by using random or systematic moves and/or modifications of the blocks, and a comparison of calculated and observed diffraction patterns and/or other cost functions (CF) such as crystal energy, atomic coordination *etc.* Based on the »fitness« of the current structural model, decisions are made on how to improve the model. Generally speaking, this is a global optimization problem of great complexity. Two algorithms of global optimization have found wider application in the SDPD.

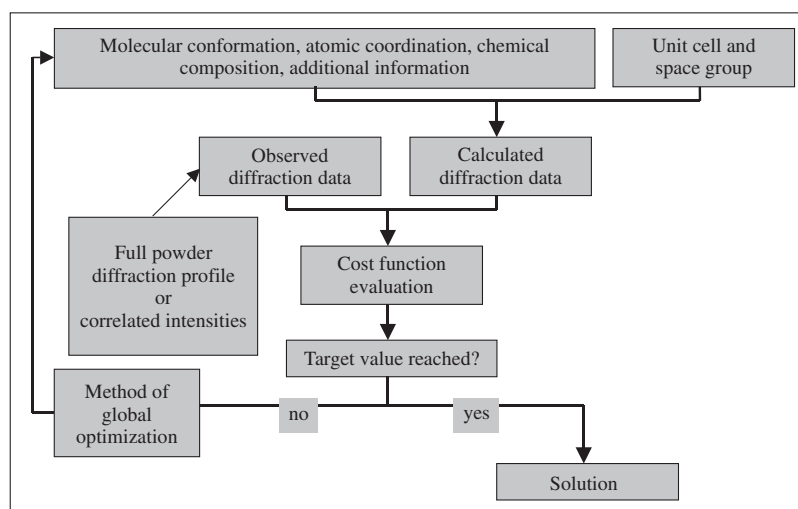


Figure 2. A typical flow chart of a direct space method as applied to SDPD, the case of the FOX program.³⁴

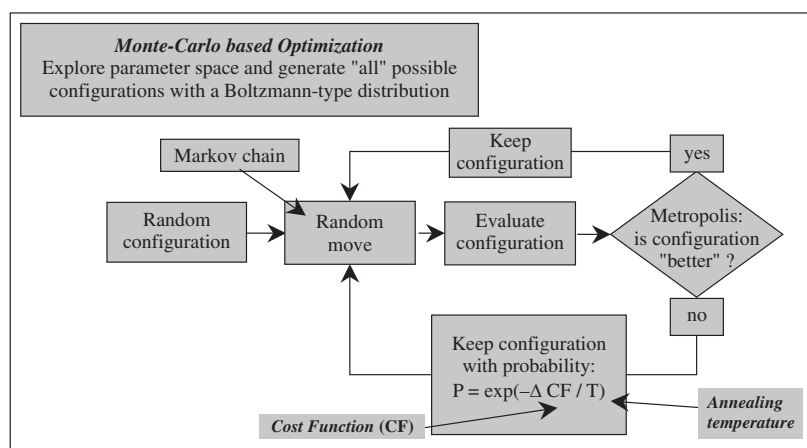


Figure 3. Flow chart of the Metropolis algorithm²⁹ of simulated annealing as applied to SDPD.

Simulated Annealing and Parallel Tempering. – SA and PT algorithms are both based on MC sampling, earlier known as "statistical sampling" (for review, see Newman and Barkema²⁸). The first, and now widely used, algorithm of the MC sampling is based on the Boltzmann distribution, and is known as the Metropolis algorithm.²⁹ The MC sampling as applied in SDPD is also called the Reverse Monte Carlo,³⁰ because the system is modified by random changes under the constraint of the observed data, like the diffraction pattern. A flow chart of the Metropolis algorithm applied to SDPD is given in Figure 3.

Evolutionary Theory – Genetic Algorithm. – Computing using GA, a fast developing tool of science and technology, is helpful in solving multi-parameter optimization tasks. GA forms a subset of broader classes of global-optimization strategies called population-based methods, and evolutionary algorithms. The concept of GA follows the old idea of minimizing human efforts in solving difficult scientific and technical problems by learning from

the nature (see Holland³¹ or Goldberg³²). Genetic computation proceeds in the space of (usually binary coded) variables. It mimics the evolution of living organisms represented by the points in this space (trial solutions). At the beginning, a population of individuals (called also chromosomes, agents...), which may represent trial solutions of the optimization task, is generated. Next generations are successively created using simplified principles of plant or animal (Darwinian) evolution. The calculation is terminated by application of a suitable stop condition. The basic genetic operators used in the formation of each new population include selection, crossover and mutation. GA was first used for SDPD in (Shankland *et al.*⁵ and Kariuki *et al.*³³). A flow chart of the genetic algorithm applied to SDPD is given in Figure 4.

FOX: Free Objects for Xtallography. – At the end of the last century, direct space methods were developing intensively in the field of molecular crystals. Significantly less activity was found in the domain of non-molecular

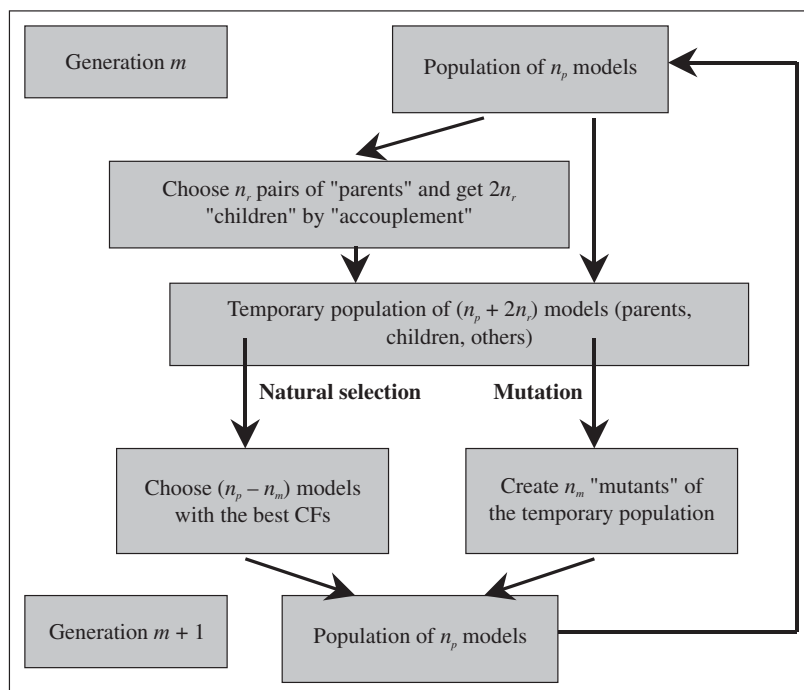


Figure 4. A general flow chart of the genetic algorithm as applied to SDPD.

(inorganic) crystals. However, the idea of constructing the crystal structure from well defined building blocks, like molecules in the case of molecular crystals, can be applied also to the non-molecular crystals such as extended solids or framework structures. And this was the main idea behind FOX,³⁴ which has become a friendly tool for solving not only non-molecular but also molecular structures from powder diffraction data.

Any crystal structure can be described in FOX as a combination of scattering objects, which can be independent atoms, molecules, polyhedra or molecular fragments such as amino acids. The advantage is that by an adequate choice of geometrical descriptors that characterize the crystal structure, the number of free parameters to optimize the degree of freedom (DoF) can be decreased. The non-molecular crystals can be built up from different building blocks such as coordination polyhedra, monoatomic layers or structural sheets of finite thickness. The easiest way is to construct the crystal structure, if possible, from coordination polyhedra. A wide range of polyhedra is available in FOX (tetrahedron, octahedron, cube, prism, square plane, icosahedron), and these are naturally described using bond distances, angles and dihedral angles. They were originally described using the Z-matrices like for molecules³⁴ to keep the uniform description for all building blocks in FOX. The description was later changed to the restraint-based approach³⁵ to avoid some pitfalls of the Z-matrices, however, with less benefit for the non-molecular compounds.

To describe a crystal structure adequately, it is necessary to take into account the possibility of corner-shar-

ing between polyhedra, which is done in FOX by the dynamic occupancy correction (DOC), which also handles special positions.³⁴ DOC was shown to be very powerful in the case when the exact composition of the studied compound is *a priori* not known exactly, like hydrogen in metal hydrides obtained by the hydrogen absorption in a metallic matrix of an alloy or intermetallic compound.

Any CF used in addition to the diffraction data can be valuable to find the correct structure, either to find the global minimum or to disfavour unsound configurations and thus reduce the overall parameter space to be sampled. Because of non-uniqueness of the energetic description of atomic interaction in crystal structures, we have preferred to implement in FOX a simple anti-bump (AB) CF that adds a penalty when two atoms are closer than a minimum distance. This minimum distance can be input by the user for each pair of atom types. For identical elements, this function also allows DOC to merge the atoms (when the distance tends toward zero), so that for identical atom types which completely overlap, the penalty decreases to zero.

Since its release in 2001, FOX has been quite often used for solving non-molecular structures from powder diffraction data (for a review see Černý and Favre-Nicolin³⁶). The complexity of structures solved by FOX ranges from 2 to 34 independent atoms found *ab-initio*. Decreasing the DoF by modeling the structure with larger building blocks was one of the reasons for using FOX for SDPD of non-molecular compounds. In many cases, the tetrahedral and octahedral units have been successfully used.

Fox is an open-source software, released under the GNU General Public License. It can be downloaded from <http://objcryst.sf.net/Fox>. Precompiled versions are available for windows and MacOS X. Future developments of FOX do not depend only on its authors, but since FOX is available as an open-source program, also on any user who decides to contribute modifications.

CONCLUSION

Structure determination of non-molecular compounds from powder diffraction data has undergone an intensive development in the last 25 years. First, applying the reciprocal space methods, which were optimized to work with lower quality data obtained from powder diffraction patterns (like programs SIRPOW-EXPO, DOREES-POWSIM and XLENS), and without an important difference when applied to molecular or non-molecular crystals. Following the pioneering works of Pannetier *et al.*²³ and mainly of Newsam *et al.*,²⁴ the direct space method has rapidly evolved and continues to be developed as a user-friendly tool for SDPD of non-molecular crystals. The main principles are again the same as for molecular crystals; however, some special tools had to be developed for treatment of special crystallographic positions, sharing of atoms between different building blocks such as coordination polyhedra, and for correct optimization of disordered atomic positions. The current (known) limits of direct space methods are around 30–40 independent atoms, and depend strongly on additional *a priori* knowledge about the building blocks of the crystal structure.

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SAŽETAK

Utvrđivanje kristalne strukture nemolekulskih spojeva primjenom difrakcije u prahu

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U radu se daje pregled metoda za određivanje kristalne strukture nemolekulskih spojeva (spojevi koji ne sadrže izolirane molekule, većina anorganskih spojeva, intermetalni spojevi i dr.) primjenom difrakcije u prahu. U prikazanim metodama struktura se određuje izravno u realnom prostoru ili u recipročnom prostoru. U metodama koje se odnose na recipročni prostor upotrebljavaju se algoritmi koji su poznati u određivanju strukture jediničnog kristala (direktne metode, Pattersonova sinteza) te zahtijevaju razlaganje difrakcijske slike praha u pojedinačne maksimume. U metodama koje se odnose na realni prostor nije potrebno razlaganje difrakcijske slike praha. Te se metode temelje na modifikaciji strukturnog modela u cilju poboljšanja slaganja između uočene i izračunate difrakcijske slike. Prikazani su dostupni računalni programi koji se primjenjuju u metodama za određivanje strukture u realnom prostoru.