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Crystal Structure Solution from Powder Diffraction Data – State of the Art and Perspectives*

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An overview of contemporary methods of crystal structure solution from powder diffraction data is given. Methods are compared with respect to their advantages and disadvantages. A choice of an appropriate method is discussed in the light of understanding the structural problem to be solved. The need of the variety of methods for the variety of problems is illustrated by examples. Some directions of possible future development are discussed.

INTRODUCTION

Structure solution from powder diffraction data has been a very popular topic among crystallographers in the last few years. Before the end of 1979, about 10 non-trivial structures were determined from powder data. This number grew to about 50 by the end of 1990 and there were more then 200 such reports by the end of 1996. In the last three years, the annual number of structures solved from powder data was over 50. Another illustration of the popularity of the topic is from the recent 5th European Powder Diffraction Conference, where 3 of 10 plenary lectures were devoted to structure solution from powder data[1–3] and about 10 novel structures were reported at poster sessions.

A question which arises in connection to this intense development of the method is: why did it not happen before? The basic interest was continuously present – there were always many interesting materials that could

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not be prepared in the form of suitable single crystals. And the powder methods (re)started their development after waiting for so many years.

In my opinion, this delay was necessary to develop powder diffractometers and also fast computers to the current state. Only the contemporary high-resolution and high-accuracy diffractometers can provide data which are good enough to attack the problem on a more routine basis. The development of instruments was parallel with the development of a full-profile refinement technique called the Rietveld method[4] which can extract maximum information from the powder diffraction pattern. Once it became possibile to obtain reliable structural information from an approximate initial structural model by Rietveld refinement, the realization of the idea to use the same data for obtaining the initial model started.

Currently, one has a good chance to solve a structure of about 15–20 atoms in the asymmetric unit,[5] and even a trial to solve a structure with up to 50 atoms in the asymmetric unit may be rewarded with success.[6,7]

In this paper, the basic principles of the current by most used methods for structure solution from powder data are presented. Methods are classified on the basis of the steps needed to come from the powder pattern to the final structure.

STRUCTURE SOLUTION FROM POWDER DATA – THE STEPS NEEDED

The procedure of solving a crystal structure from powder diffraction data can be divided into the following steps:

- data collection,
- indexing,
- space group determination,
- pattern decomposition (not for all methods),
- structure solution
- completion of the structure (if the initial model from the previous step is not complete),
- final refinement.

Contrary to the procedure with a single crystal, decisions at various steps are usually not unique and as a result the steps can be heavily intermingled. A commonly accepted rule of the correctness of the results in single steps of the structure solution is that only a successful final refinement confirms the results of all previous steps.[8] When a good fit with a chemically reasonable model is achieved, one can trust the structure. Many comparisons with single crystal results have shown that the positional parameters determined from powder are close within standard deviations to those determined from single crystals.[9,10] Atomic displacement parameters are less reliable.

Data Collection

The powder diffraction data from which the structure solution is intended must be of the highest possible quality. This means the highest possible resolution, excellent angular accuracy and accurate intensities. For high resolution, the use of small slits and large diffractometer radii are needed, which requires a compromise to achieve a reasonable intensity (counting time). Synchrotron source based diffractometers can reach better resolution mainly due to the high intensity of a primary beam, which allows for a very efficient single-wavelength monochromatization and large diffractometer radius. To illustrate the role of the resolution, three powder patterns of the same material (($(C_2N_2H_9)[MnPO_4] \cdot H_2O$) are compared in Figure 1. It is evident that the synchrotron data contain more information than the other two data sets.

Modern diffractometers, if carefully maintained, provide reliable angular accuracy. With certain geometries (Debye-Scherrer and Bragg-Brentano

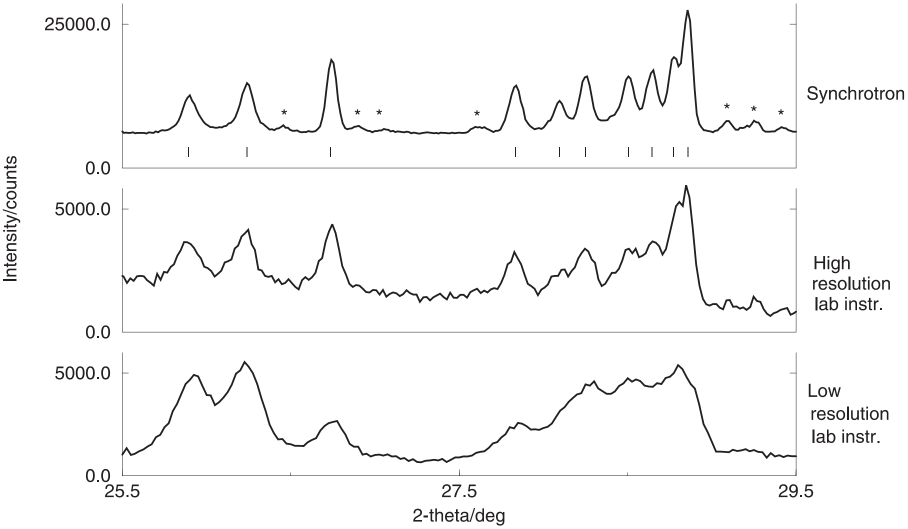

Figure 1. A comparison of three powder diffraction data sets of the same compound (monoclinic $(C_2N_2H_9)[MnPO_4] \cdot H_2O$), collected with three different instruments (λ = 1.5406 Å in all cases). Note the importance of high resolution for correct determination of the number of reflections contributing to the observed maxima, their positions and intensities. Small maxima denoted by * belong to different impurities (manganese oxides and phosphates).

with divergent beam, for example), a careful mounting of the sample is also crucial to obtain accurate diffraction angles.

Reliable intensities are most difficult to obtain. The size of the crystallites should be optimal, absorption should be taken into account for the capillary measurements, preferred orientation and surface roughness should be avoided for flat plate geometry.

Slits should be chosen so that the scattering from a constant volume of material is detected over the whole angular range (fixed slits with flat plate geometry).

Indexing

In the powder pattern only the information of interplanar spacings and no information on the angles between crystal planes are present. Therefore, indexing is in principle a trial-and-error procedure and the correctness of the unit cell found is based exclusively on the exact match of the calculated and observed peak positions. This is of course possible only for a pattern with excellent angular accuracy. In the case of large, low symmetry unit cells, high resolution is also necessary to distinguish peaks in overlap.

For example, it is quite evident that the overlap in the case of a low resolution laboratory instrument, as shown in Figure 1, is too high to extract accurate positions of sufficient number of peaks to index the pattern. The high resolution laboratory instrument and synchrotron data sets were much better in this respect and the indexing was unambiguous (monoclinic, $a = 21.974$ Å, $b = 9.367$ Å, $c = 6.663$ Å, $\beta = 90.94°$).

The most frequently encountered problems which prevent indexing are the presence of impurities and poor crystallinity. If neither of these is present, unit cells of volumes 3000–5000 Å^3 can be determined readily. When the initial trials fail, it is advisable to try another program which uses a different algorithm.

Space Group Determination

Like in the case of single crystals, determination of the space group is based on the extinction rules for reflections. A major problem is an extensive overlap of reflection positions at higher diffraction angles, which prevents finding out which reflections are absent. Usually, one can only be sure about the absence of a very limited number of single reflections at low angles. It is thus a very common situation that for a given powder pattern several space groups are possible. For example, in the monoclinic system it is even difficult to distinguish between $P2_1/c$ and the groups $A2$, Am and $A2/m$, which have the same extinction rules, as given in Figure 2 for the pattern of $C_7F_{15}COOH$. It can be seen that extinction rules are similar for

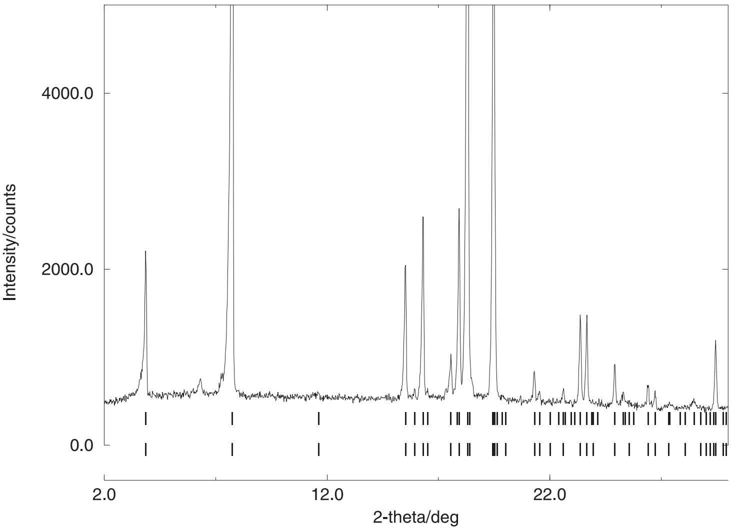

Figure 2. An ambiguity in assigning a space group for monoclinic phase ($C_7F_{15}COOH$). Upper bars represent allowed reflection positions in $P2_1/c$ and lower bars are consistent with space groups $A2$, Am, $A2/m$. Extinction rules are equal for the first few isolated reflections while the overlap at higher angles prevents an unambiguous decision.

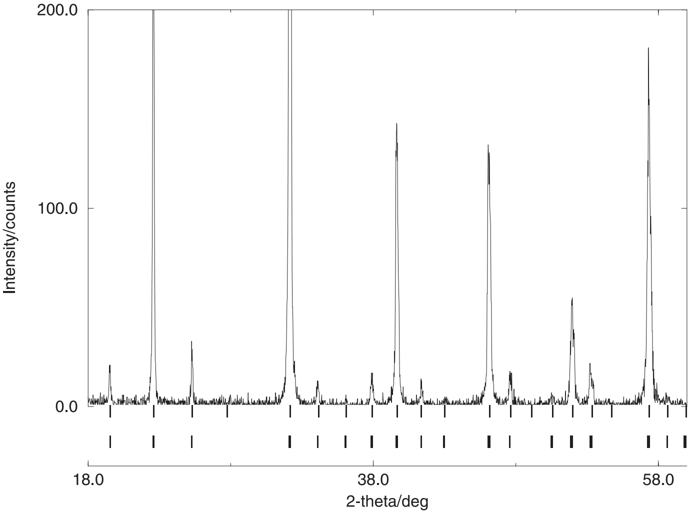

Figure 3. Indexing and space group determination of $La(Mg_{0.5}Ti_{0.5})O_3$. The upper vertical bars represent reflection positions of a cubic unit cell (a = 7.862 Å, primitive, space group impossible to assign) and the lower bars are for an orthorhombic unit cell (a = 5.561 Å, b = 5.574 Å, c = 7.862 Å, space group Pbnm). Cu $K\alpha_1$ radiation (λ = 1.5406 Å) was used.

the very low angle reflections, while it is not possible to look for differences at higher angles due to extensive overlap. In such a case, there is no other way of finding the correct space group than trying all possibilities and the best solution would show which is the correct one.

A further example also shows how one usually has to return to earlier stages in the structure solution process to correct wrong decisions in previous steps. The powder pattern of $La(Mg_{0.5}Ti_{0.5})O_3$ was initially indexed as cubic (a = 7.862 Å). All reflections were indexed and there were some extinct reflections (Figure 3). The problem arose when none of the cubic space groups was consistent with the observed extinctions. After detailed examination of the pattern, broadening of some peaks was detected and indexing with an orthorhombic space group *Pbnm* (a = 5.561 Å, b = 6.574 Å, c = 7.862 Å), which is common for this class of ceramics, was tried. The a and b cell parameters are so close to each other, and multiplied by $\sqrt{2}$ so close to c, that there was no splitting of the reflections expected for the orthorhombic cell. The broadening, however, corresponded to the positions of split peaks (Figure 3). Final refinement confirmed the orthorhombic indexing.

Powder Pattern Decomposition

The aim of the pattern decomposition is to extract a »single-crystal-like« data set from the powder pattern. With such a data set one can apply all methods which are in use for single crystals – of course having in mind large errors in the extracted intensities. These errors are caused by the overlap of reflections. It is especially at high diffraction angles that there are many reflections that contribute to the intensity of a single observable peak in the pattern. A usual treatment of such groups of reflections under one diffraction peak is to give them equal intensity – equipartitioning.

The extraction itself consists of fitting the powder pattern by varying the unit cell parameters, profile parameters and intensities of allowed reflections in the assumed space group. Two most frequently used approaches are Pawley's[11] and LeBail's.[12] The former treats intensities as individual variables in the least squares fitting – so that some of them can easily become negative, which is not physically reasonable. To improve this feature, Bayesian statistics[13] is used and it gives significantly better results.

LeBail's procedure is an iterative redistribution of initial intensities. Intensity of each point in the pattern is distributed among the contributing reflections, taking into account the profile of reflections. The advantage of this method is that it can start either from an unbiased model (all intensities initially set equal to 1) or a biased model (initial intensities calculated from a partial structural model). The former possibility will automatically lead to equipartition of overlapping reflections, while the latter will give a data set with better partitioning (distribution of the intensities of reflections contributing to a single observed diffraction maximum is better).

The biased model can thus be used as a feedback in an iterative solving process. The unbiased extraction is used to obtain a starting rough structural model, and this model then improves the extracted intensities which give a better model, and so on.

Pattern decomposition is not necessary for all methods of structure solution from powder data, as it will be discussed later.

Structure Solution

Before applying any method for structure solution from powder diffraction data, one has to index the powder pattern and determine the space group and unit cell content. After that, the diversity of methods, presented in a separate chapter (Methods for Structure Solution from Powder Diffraction Data), is at one's disposal. The result of structure solution could be a complete structural model or just a part of it, depending on the complexity of the structure and the data quality.

Structure Completion

When only a partial structural model is obtained in the solving procedure, one can choose several ways to complete the structure. Some solving methods allow recycling – like the biased extraction mentioned above. There are two most commonly used approaches, which are independent of the method used, to obtain the partial structural model. One is geometrical modeling and the other is Fourier recycling, which works the same way as in the case of single crystal data – the only difference is of course the sharpness of the Fourier maps. Usually, both are used together and may be also combined with a partial Rietveld refinement.

Refinement

When the structural model is complete, the structural parameters are fitted to achieve as good fit of the calculated powder diffraction pattern to the observed pattern as possible – keeping the structural model chemically reasonable. In the early stages of the refinement, damping of the calculated shifts and restraints of bonds and angles are commonly used. In the final cycles, damping and the restraints should be released. Sometimes it is necessary to keep some restraints to stabilize the refinement, however.[14] In the final cycle, the serial correlation should also be avoided by diluting the pattern (using only every n-th point in the pattern, n is usually 3–9) in order to obtain more realistic standard deviations.[15]

METHODS FOR STRUCTURE SOLUTION FROM POWDER DIFFRACTION DATA

It is not the purpose of this paper to give details of every method or variation of a method that is currently in use. The methods are too numerous and too different in the approach to the problem. Only the basic principles of the major routes from the initial data to the structural model are presented and some interesting variations discussed. To help the presentation, the methods are ordered in the scheme in Figure 4. The ordering is based on the steps applied in each method to come to the solution. The scheme also helps find common points in different routes.

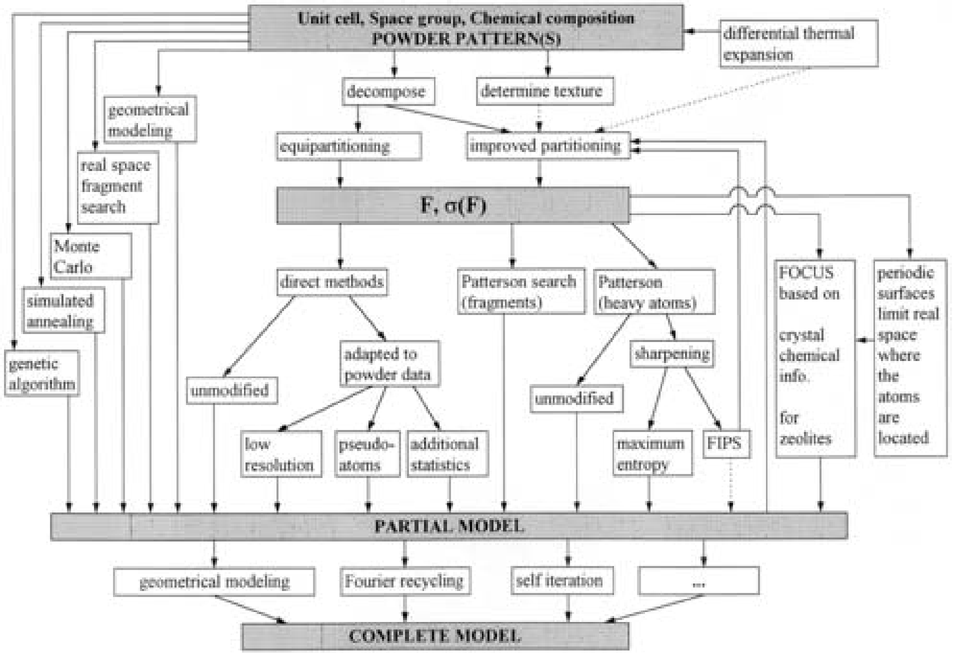

Figure 4. A schematic ordering of methods for structure determination from powder diffraction data. Methods (in white rectangles) are ordered with respect to the pathway from the data to the structure (gray rectangles).

Direct Space, Pattern Reference Methods

The methods in this group comprise: geometrical modeling, real space fragment search, Monte Carlo method, simulated annealing, and genetic algorithm. These methods differ in their origin, approach and additional sources of information they use. They are grouped together because of two important common features: 1) they try to find a real-space structural model, 2) they use the powder pattern as a reference to classify the models found. This results in avoiding the extraction of individual reflection intensities from the pattern.

Geometrical modeling comprises all techniques that use either specific known structural data (fragment, molecule, conformation) or just crystal chemical information (expected bond lengths and angles) in order to build a model which conforms to all the known data, including the unit cell, space group and cell contents.

The tools used to build such a model range from hands (manual model building) to a 3D real-time moving computer graphics. In its manual version, it is one of the oldest methods while the basic idea of the method – using the known structural information – can be exploited very efficiently by modern tools.

To illustrate this technique, an example of a structure solution using this approach is given.[16] The powder pattern of a cyclo-β-tetrapeptide with the (*R,S,R,S*) configuration, derived from 3-aminobutanoic acid (Figure 5) could be indexed as tetragonal and a possible space group was $I\bar{4}$ (No. 82). From the known density, it was calculated that only 1/4 of the molecule represents the asymmetric unit. Since the molecule itself can possess a fourfold inversion axis, it was clear that the principal axis of the space group passes through the molecule. Since the conformation around the peptide bond is rather rigid and close to planarity, it was only necessary to compose a monomer and place it into the unit cell so that the symmetry generated equivalents made the whole cyclic tetramer. The orientation of the tetramer was established by avoiding too close contacts between molecules and considering the comparison of the calculated and observed powder patterns.

The model obtained in this way was successfully refined and the material appeared to be very interesting – it possesses nanotubular stacks parallel to one another (Figure 5).

Real space fragment search also uses a known structural fragment (which can also be a whole molecule). The aim is to find the actual position and orientation of the fragment in the unit cell. There are two basic approaches to achieve this: a) an exhaustive search through all possible positions and orientations, b) moving the fragment by »trial and error« procedure with certain criteria which promote »successful« moves. One example of such a procedure is the Monte Carlo method described below.

Monte Carlo method is the name of a »trial and error« algorithm which is widely used in many fields of science. As a tool to solve a crystal structure it may use known information (*i.e.* fragment) or need not do it[17]. The procedure starts with a random structure (or position of the fragment) and then calculates random atomic moves (or fragment moves). Before a

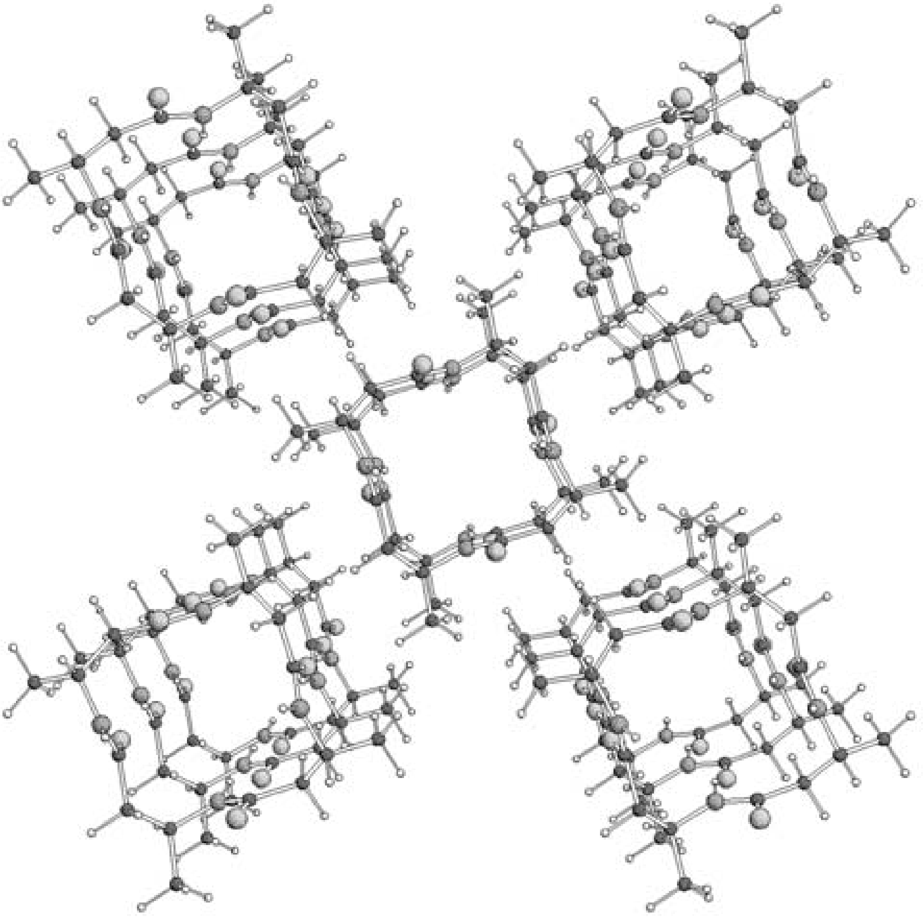

Figure 5. A perspective view through the nanotubular structure of the (*R,S,R,S*) cyclo-β-tetrapeptyde of 3-aminobutanoic acid. The rings are interconnected by hydrogen bonds to form tubes. See Ref. 16 for details.

move is accepted, a »successfulness« test is made. This test consists of refining the scale factor of the calculated pattern with moved atoms. If R_p is lower than the present, the move is accepted – atoms (fragments) are actually moved to new positions. Even if R_p increased, the move may be accepted with some probability. This enables the algorithm jumping out of the local minima and finding the global one.

To find a correct solution, many trials are required and the true solution is usually recognized from a plot of R_p *vs.* trial. The lowest R_p (usually significantly lower than the rest) indicates the true structure.

Simulated annealing is similar to the Monte Carlo method. It differs in the way of accepting moves, it adds one or two additional criteria.[18] The one that is essential for this method is that large moves are accepted at the beginning of trial (simulating high temperature) and afterwards smaller and smaller moves are allowed (annealing). Additional criteria are based on the crystal chemical information (expected bond lengths and angles), the moves which produce a more »sensible« structure are promoted.

Genetic algorithm is a very fashionable algorithm used in programming expert systems in many fields of science. It involves the idea of miming the evolution of living organisms which produces more and more successful individuals by cross-breeding and mutations.

The algorithm consists of the following steps:

- definition of genes which is in fact »splitting« an individual (which represents a »complete solution«) into a definite number of »properties« – genes – in which individuals may differ;
- creating a starting population – a number of initial »solutions«;
- defining the selection criteria – a reference to which the individuals will be tested and ranged by »successfulness«;
- defining the mutation frequency – how often an existing gene is randomly changed;
- cross–breeding – producing new individuals by exchanging a number of genes between two individuals producing two new individuals (the number of exchanged genes varies); more successful individuals are allowed to cross-breed more often;
- after a number of generations (cross-breeding cycles), the most successful individual (not necessarily in the last generation) is declared as the correct solution.

Early attempts to use this algorithm for structure solution failed because of the »combinatorial explosion«. Namely, if each fractional coordinate of atoms in the asymmetric unit is regarded as a gene, the number of all possible combinations of such genes quickly reaches immense numbers and the correct solution will just never be found, even with fastest computers.

In order to keep the problem manageable, the number of genes has to be small (below 10). Recently, a successful use of this algorithm was demonstrated on organic molecules with rigid fragments where only some torsion angles were free.[19] Genes were defined as the coordinates of the center of mass (3 genes) and torsion angles around flexible bonds (up to 5 more genes). The appropriate starting population was found to be between 50 and 100 individuals, the frequency of mutations was 1 per approximately 100 breeding cycles and about 10000 generations were needed to find the correct solution.

Advantages of these five methods are the possibility to find a global minimum, the unnecessariness to extract intensities from the powder pattern and their readiness to incorporate known structural information.

The disadvantage is the computing time, which increases rapidly with the complexity of the structure.

Direct Methods

Direct methods are a well known and very successfully used tool for structure solution from single crystal data. They can also be applied using the extracted intensities from the powder pattern. With unmodified programs using direct methods it is generally possible to solve only simple structures with a small degree of reflection overlap in the powder pattern. Therefore, many groups doing crystallography are trying to adapt the direct methods to enhance their ability in the case of powder data.

One quite prominent direction is explored by the group of Giacovazzo, who implemented the use of additional statistical relationships that are applicable only to the intensities extracted from the powder pattern and are absent in single crystal data sets.[5] A recent development in this direction is adding an automatic recycling possibility to the algorithm.[20] The procedure starts with an equipartitioned data set, finds a partial model and uses it to improve partitioning, which, in turn, improves the model as described in section Powder Pattern Decomposition.

If the structure consists of known rigid fragments, the whole fragment can be replaced by a »pseudo-atom« having the scattering power equivalent to such a fragment.[1] The simplest use is just to use a heavy atom with the same number of electrons as present in the fragment with a large displacement parameter; a »pseudo-atomic« scattering factor can, however, also be calculated and applied for the fragment. The number of atoms to be found by direct methods is thus reduced significantly and the possibility of finding a structure by direct methods increases correspondingly. Furthermore, the resolution limit can be lowered if only some large fragments are to be located, like in the case of proteins.

The benefit of lowering the resolution (which means using only the low angle part of the powder pattern) is that the reflection overlap is usually small at low angles and thus the intensities of low angle (low resolution) reflections are well defined. Using a modified direct method approach on a small number of well defined low resolution reflections may reveal heavy scatterers in the structure if the distance between them is larger than the resolution limit. This idea is explored for the case of zeolites where the distance between tetrahedral atoms is about 3.1 Å, so that only the reflections with higher *d* values could be necessary to find the positions of these atoms.[21]

Patterson Based Methods

These methods in their basic appearance are also well known among crystallographers and also successfully used with the single crystal data. Like direct methods, they can be applied unmodified using the extracted intensities. Due to the poor quality of these intensities, the Patterson maps produced are diffuse and often insufficient to solve the structure. Two methods of sharpening the Patterson map, which are successfully used to solve crystal structures, are included in Figure 4.

The maximum entropy approach[22] is a rather complicated technique to sharpen all kinds of images. It applies the statistics-based equations on the pixels in the image and produces a sharp image from a diffuse one. It is also used, for example, to sharpen images from satellites. If applied on the diffuse Patterson map, it may produce a map which is sharp enough to show the positions of heavy atoms which was not the case before the treatment.

The Fast Iterative Patterson Squaring (FIPS)[23] does not aim only at sharpening the map. It combines the squaring of the Patterson map with a statistical comparison of the intensities of non-overlapping (well defined) reflections versus the intensities of overlapping (ill-defined – equipartitioned) ones. During iteration, the algorithm redistributes the intensities of overlapping reflections so that the statistics of both classes of reflections becomes similar. In fact, this means an improved partitioning of the overlapping reflections, which also results in a sharper Patterson map, and can be used to enhance any other method using the extracted intensities.

Active Use of Crystal Chemical Information

Some classes of materials have many structural features that are present in all members of the class. One of these classes are the microporous materials based on the three-dimensional frameworks of tetrahedrally coordinated heavy atoms (Si, Al, P, Ga, Zn...) linked by oxygens. Focusing only on the heavy atoms, it follows that each of them has 4 heavy neighbors at a distance of about 3.1 Å, which tetrahedrally surround the central one. Based on this crystal chemical information, the FOCUS[24] program was developed to solve crystal structures of microporous materials. The program algorithm is shown in Figure 6. It uses extracted structure factors from pattern decomposition and random phases to calculate an electron density map. This map is then searched for peaks and the peak list can be used in two ways: 1) assigning atoms to peaks based on the intensity, 2) trying to find a subset of peaks which form the 3D tetrahedrally connected fragment and then assigning atoms. In both cases, the assigned atoms are used to test if they represent a topology (4 connected tetrahedral network which represents a »possible« structure). If a topology is found, it is just written to a file and the program continues. Next step is the calculation of a new set of

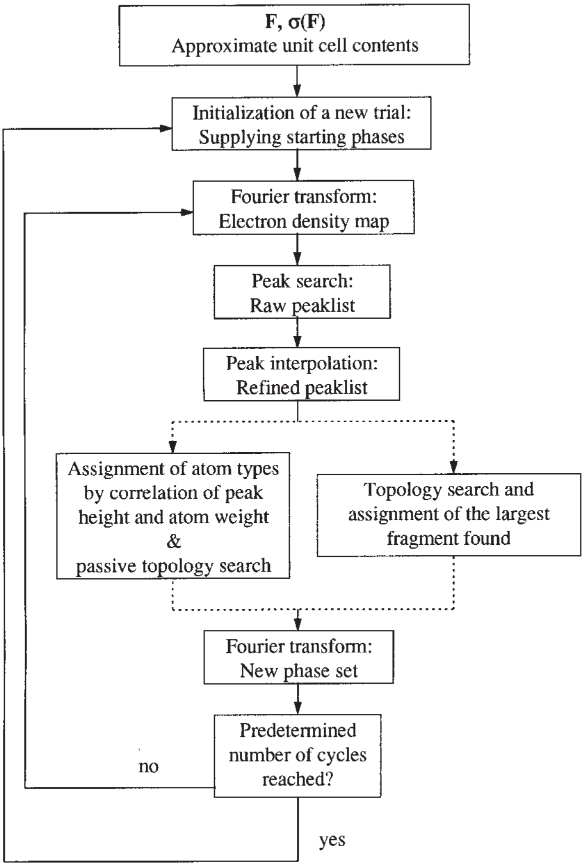

Figure 6. A schematic representation of the FOCUS algorithm. The crystal chemical information is incorporated in the term "Topology search" (see text and Ref. 24 for details).

phases from the assigned atoms. These phases are then used to calculate a new electron density map and the procedure is repeated for a predetermined number of cycles. Then, a new trial with another set of random phases starts. After an appropriate time, when sufficient (or not) frameworks are found (one hour to several days on a fast computer) the user stops the program and all the frameworks found are compared. The one that appears most frequently is the correct solution.

As an example of a typical structure where the FOCUS program showed its specialized power is the aluminophosphate $AlPO_4 \cdot 2H_2O$ with the chabazite topology[25] shown in Figure 7. If this rhombohedral material is exposed to humidity, it changes to triclinic symmetry with a substantial change of

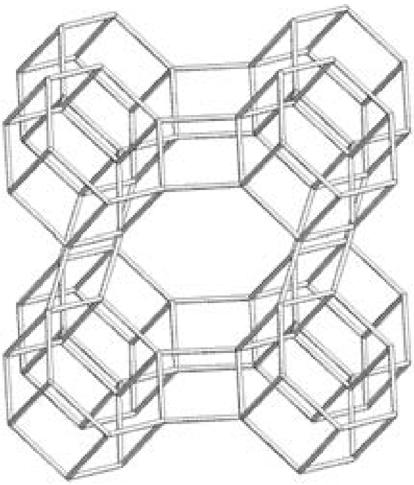

Figure 7. The topology of chabazite-like $AlPO_4$. Only the tetrahedral atoms (Al and P) are shown as equivalent tetrahedral nodes; oxygen atoms, close to the centers of connections between tetrahedral atoms, are omitted in the topology presentation. Such a structure is a typical example of a microporous material, suitable to be solved by FOCUS program. See Refs. 24 and 25 for details about the program FOCUS and topology presentation, respectively.

the unit cell parameters. The question was if the connectivity between the tetrahedral atoms was preserved or the framework interrupted. In an attempt of structure refinement with an initial model derived from the rhombohedral coordinates, it appeared that the model was too far from the real one and the trial was unsuccessful. Thus, FOCUS was given a chance to find if there was a 3D framework or not. After 2 hours running on an SGI workstation, it found a distorted chabazite framework 17 times and no other framework appeared. The model was sufficiently good to allow the refinement to proceed.

FOCUS is a good example how powerful the active use of crystal chemical information is. The disadvantage of such an approach is that it works only for a specific class of compounds.

Periodic Surfaces

This method is being developed in Zurich and, like FOCUS, was initially focused on the same class of compounds. During its development, it appeared that it could be used also for general structures.

The idea of this method is that a Fourier transform of only a few (one to five) strong low-angle reflections and their symmetry equivalents yields some electron density distribution in the unit cell.[26] All points with zero density form a surface which is periodic and conforms to the symmetry of the space group. This periodic surface divides the real space into two parts – a part which is »filled« (atoms are present) and a part which is »empty« (voids or intermolecular spacings). The real space where the atoms should be searched for (by any algorithm) is thus approximately halved and, which is more important, it is shaped. This means that the shape of the framework or the conformation of a molecule may be indicated by the shape of the surface – like a very low resolution electron density map. So far, this method has been only tested for microporous materials in combination with FOCUS. It was found that the CPU time needed to solve some different known structures was decreased by a factor of 100 if the space limitation imposed by the periodic surface was taken into account.

Use of Texture

This is also a new method, still under development and differs from all the methods discussed so far.[27] It aims at a perfect partitioning of the powder pattern by experimental means prior to any structural knowledge. The idea is based on the consideration that a perfectly random orientation of crystallites in a powder sample is rare and that the texture of the sample may help in partitioning the intensities among the overlapping reflections.[28]

The first step is the preparation of a strongly textured sample and then determination of its texture. Several powder patterns are then collected with different tilts of the sample which correspond to different directions indicated in Figure 8. Due to the texture, the contribution of overlapping re-

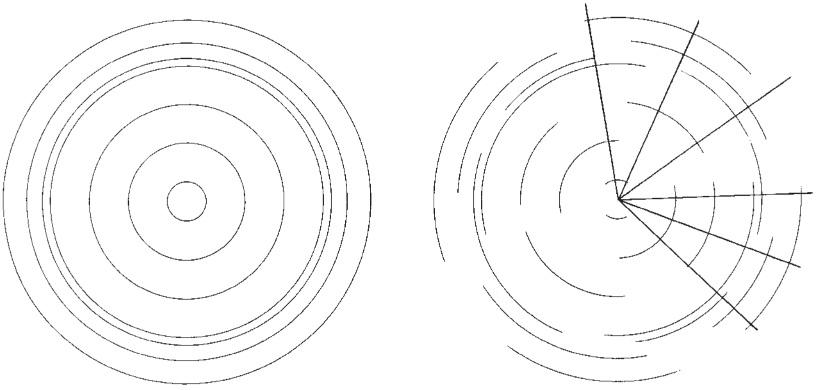

Figure 8. A schematic representation of powder patterns of a randomly oriented powder (left) and textured powder (right). While tilting has no effect in the former case, there is a significant redistribution of intensities in the latter. Straight lines represent a one-dimensional powder pattern collected at a given tilt of the sample.

flections to the observed peak intensity changes with the tilt angle, and after the texture is known, it is possible to derive the contribution of each overlapping reflection in the non-textured sample. The simulations show that the method should be able to produce a data set comparable to the single crystal one even with modest texture. How the method really works will be known after the first real measurements. This method is certainly very promising because it can correctly partition also exactly overlapping peaks (cubic case). Its disadvantage is the long collection time since many diffraction patterns are needed.

Differential Thermal Expansion

This method also improves partitioning by experimental means.[29] Here, a data set is collected at different temperatures. If the unit cell expands anisotropically, the reflections which overlap at one temperature may get separated at some other temperature. The method requires a substantial anisotropic thermal expansion coefficient and thermal stability of the material under the data collection conditions. Significant improvement of the partitioning can be obtained if these conditions are fulfilled. The disadvantage of this method is the data collection at high temperature, which is more complicated (especially regarding the accuracy of reflection intensities) than a normal room temperature measurement.

Trends of the Current (and Future) Development

It has to be mentioned that the scheme in Figure 4 does not list all existing variations of methods for structure solution from powder data, which are very numerous and have been appearing very frequently in the last years. Only the principal ideas on which the methods and their modifications are based were given to point out that each method has its advantages and disadvantages and the choice of the most successful method depends on the type of the structure in question. It is, therefore, a matter of understanding that all these methods are being developed constantly. The trends of the development thath can be deduced from recent publications and conferences are:

a) combining the existing methods to make novel, more successful pathways and feedback loops from the data to the solution;

b) including the crystal chemical information from various databases to diminish the drawback of missing information in the powder pattern;

c) utilizing fast computers to produce a lot of solutions and developing efficient criteria to extract the correct structure from the mass.

The question that arises after this survey of available methods for structure solution from powder data is: where is the limit, which is the largest structure that could be solved from powder? The answer is very difficult and one could just guess... It is quite sure that the current limits will be pushed forward substantially in the near future. How far and how quickly it depends on so many unpredictable things that I prefer to leave the answer open – the future will answer it.

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SAŽETAK

Rješavanje kristalne strukture iz difrakcijskih podataka za praškasti uzorak – sadašnje stanje i perspektive

Anton Meden

Dan je pregled suvremenih metoda za određivanje kristalne strukture iz difrakcijskih podataka praškastih (polikristalnih) uzoraka. Metode su međusobno uspoređene na temelju njihovih prednosti i nedostataka. Raspravlja se o izboru primjerene metode s obzirom na strukturni problem koji treba riješiti. Primjerima je ilustrirana nužnost primjene mnoštva metoda za različite probleme. Naznačeni su neki smjerovi mogućega budućeg razvoja.