

Combined method for *ab initio* structure solution from powder diffraction data

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Abstract

A new direct-space method for *ab initio* solution of crystal structures from powder diffraction diagrams is presented. The approach consists of a combined global optimization ('Pareto optimization') of the difference between the calculated and the measured diffraction pattern and of the potential energy of the system. This concept has been tested successfully on a large variety of ionic and intermetallic compounds.

1. Introduction

In recent decades, the determination of the atomic structure of crystalline solids has become a routine process using single-crystal X-ray diffraction. Nevertheless, even today structure determination can become rather difficult if the compound under investigation can only be prepared as a microcrystalline powder. Several methods for solving crystal structures from powder diffraction data have been developed (Harris & Tremayne, 1996; Louër, 1998; Meden, 1998). One of the first methods was developed by Rietveld (1969) in the late sixties. This approach has become an integral part of almost any powder crystal structure determination, though it actually addresses only the last step in the structure determination process consisting of five steps: (i) determination of peak positions from the raw diffraction data; (ii) indexing, calculation of lattice parameters, and determination of crystal symmetry and space group (if possible); (iii) extraction of intensities; (iv) structure solution (creation of a structural model with approximate atomic positions); (v) Rietveld refinement (refinement of the atomic positions). Steps (i)–(iii) and (v) are fairly routine nowadays, a number of computer programs being available for their implementation. Routines that extract information from diffraction data [steps (i)–(iii)] are included in many operating software packages for diffractometry [e.g. *STADIP* (Stoe), *X'pert* (Philips), *DIFFRAC^{plus}* (Bruker), *etc.*]. The Rietveld refinement method has also been implemented in a variety of programs, such as *GSAS* (Larson & Von Dreele, 1987), *FullProf*

(Rodriguez-Carvajal, 1990) and *DBWS* (Wiles & Young, 1981). They can generally be used in a fairly routine manner (McCusker *et al.*, 1999).

However, one of the main problems associated with the Rietveld method is its implicit use of local optimization of the atomic positions. Thus, it depends on the availability of a structural model, *i.e.* an approximate idea of what the atomic arrangement should be. Providing such a model from a powder diffraction pattern [step (iv) in the list above] remains a difficult task in general. In some cases, the analogy to existing compounds and their structures allows a relatively simple construction of a model, but in many other cases this is not possible.

Several approaches that address this problem have been developed since the publication of the Rietveld method in 1969. Usually, they generate a structural model '*ab initio*' (*i.e.* without any previous knowledge concerning the structure) from a powder diffraction pattern that is subsequently submitted to a Rietveld refinement. Most of these methods [especially the 'classical' direct methods (Giacovazzo, 1996), the Patterson method (Patterson, 1934) and the method of maximum entropy and likelihood (Bricogne, 1991), but also some other approaches, *e.g.* *FOCUS* (Grosse-Kunstleve *et al.*, 1997)] consider intensity values for each reflection (*hkl*), more or less in analogy to single-crystal methods. Unfortunately, the extraction of the intensities *I(hkl)* from the experimental diffraction pattern *I(2θ)* as a function of the scattering angle *2θ* quite frequently poses serious problems because of the ambiguity arising from the intensity overlap of different reflections (*hkl*) at the same value of *2θ*. Though a variety of sophisticated techniques (Pawley, 1981; Le Bail *et al.*, 1988) have been developed for the extraction of *I(hkl)* from overlapping reflections, it may be difficult to determine these intensity values with sufficient accuracy for the 'classical' methods to be applicable. The so-called 'direct-space methods' avoid this problem by proposing structural models independent of the powder diffraction diagrams (Harris & Tremayne, 1996; Louër, 1998; Andreev *et al.*, 1997; Harris *et al.*, 1998; Shankland *et al.*, 1997). Such a model is subsequently validated by comparing the

calculated and the experimental powder patterns with respect to $I(2\theta)$. These values are readily obtained from experimental powder diffraction data of sufficient quality.

In general, direct-space methods work as follows. Beginning with some arbitrarily chosen starting configuration, the difference between the calculated and the measured diffraction patterns $\Delta I_{\text{exp/calc}}(2\theta)$ (cost function) is minimized through a repeated change of the atomic arrangement while the unit cell is kept fixed. If no other constraints are introduced, this straightforward prescription [also known as the ‘Reverse Monte Carlo’ method (Kaplow *et al.*, 1968; McGreevy, 1997)] is in practice limited by the fact that for most crystalline solids the system quickly becomes trapped in some minimum that does not correspond to a physically reasonable atomic arrangement. The reason for this lies in the ‘landscape’ of the cost function, which includes numerous deep local minima (McGreevy, 1997). In order to avoid these traps, certain additional constraints are required, which restrict the available configuration space to physically reasonable atomic arrangements.

Fortunately, the physically reasonable region of configuration space has been the subject of investigation in the field of crystal structure prediction (Catlow *et al.*, 1994; Bush *et al.*, 1995; Schön & Jansen, 1996). Nearly all of these methods use optimization of the atomic arrangement with regard to elaborate cost functions [mostly potential energy (Bush *et al.*, 1994; Schön & Jansen, 1994, 1995; Battle *et al.*, 1995; Putz *et al.*, 1998), but also deviation of crystal chemistry rules (Pannetier *et al.*, 1990) and others] in order to detect the global minimum and hence the crystal structure of the system. Furthermore, some approaches (Schön & Jansen, 1994, 1995) extend the global optimization to the shape and content of the unit cell.

Unfortunately, most methods for structure prediction still suffer from the lack of really adequate cost functions. Nevertheless, they might be of use even at their current state concerning the problem of crystal structure determination from powder diffraction data, if these data and the knowledge of the unit cell and its content are regarded as additional information for the global optimization.

2. Method

2.1. Concept

In order to avoid the traps mentioned above, our concept for crystal structure solution from powder patterns consists of a combined global optimization (‘Pareto optimization’)† of the difference between the

† The idea of a combined optimization of two (or even more) cost functions (‘multi-objective’ or ‘multicriteria’ optimization) was first developed by V. Pareto in the field of economics in the late 19th century (Pareto, 1896/97).

calculated and the measured diffraction pattern and of the potential energy of the system. Size, shape and content of the unit cell are assumed to be known from experiment.

‘Merging’ both hypersurfaces‡ weakens or even eliminates the minima that belong to only one of the two surfaces, and strengthens those which belong to both of them. Therefore, a sufficiently long global optimization run should sooner or later reach the global minimum of the system corresponding to the correct crystal structure.

The combined cost function C is calculated as

$$C = \alpha E_{\text{pot}} + (1 - \alpha) R_B, \quad (1)$$

where E_{pot} is the potential energy of the atomic arrangement (*cf.* §2.3) and R_B denotes the so-called R value (Harris & Tremayne, 1996) frequently used for the comparison of calculated and experimental diffraction patterns (*cf.* §2.3). α is the Pareto parameter which weights the contributions of the two parts of the cost function. The best choice for α may vary from problem to problem. This parameter can be used to weaken the influence of either a low-quality diffraction pattern or a very crude potential on the overall cost function. Thus, a powder pattern in which the intensity values are suspected to be not very accurate may be balanced by a good potential by choosing a larger α value, and *vice versa*. Nevertheless, a value of $\alpha = 0.5$ has been shown to be a good starting point for most systems.

2.2. Simulated annealing

As mentioned above, the atomic arrangement representing the solved crystal structure is supposed to correspond to the global minimum of the multi-dimensional hypersurface of the cost function. Hence, a global optimization method operating on the atomic coordinates should be able to solve the structure. One of the most common algorithms for global optimization is the so-called ‘simulated annealing’ algorithm (Kirkpatrick *et al.*, 1983). The great advantage of this method lies in the relative ease of implementation and the very general applicability, more or less regardless of the specific optimization problem. Simulated annealing is a Monte Carlo method based on the Metropolis algorithm (Metropolis *et al.*, 1953) which implements a weighted random walk through configuration space.

Starting from a current configuration i , a neighbouring configuration $i + 1$ is chosen at random according to a set of rules (‘move class’). If the cost function C_{i+1} is below or equal to C_i , the move is always accepted, *i.e.* $i + 1$ becomes the new current configuration. Otherwise, the move is only accepted with probability $\exp[-(C_{i+1} - C_i)/K]$, where K is a control

‡ Both cost functions depend on all atomic coordinates in the fixed unit cell.

parameter of the random walk. Thus, during a sequence of such Monte Carlo steps, the system can climb over barriers of the hypersurface of the cost function, depending on the control parameter K . In analogy to the parameter 'temperature' in the annealing of a real material, starting from a relatively high value the control parameter is slowly reduced according to a certain schedule (the so-called 'temperature program'), until the system ends up in a deep-lying minimum. It can be shown that an ergodic system will reach the global minimum during such a simulated annealing run for $t \rightarrow \infty$ (van Laarhoven & Aarts, 1987; van Laarhoven, 1988).

2.3. Potential-energy calculation

In principle, any method for the calculation of the potential energy E_{pot} can be employed, but the global optimization usually makes *ab initio* energy calculations not feasible. With regard to those test structures that can more or less be considered as ionic compounds, a simple empirically parametrized two-body potential is chosen:

$$E_{\text{pot}} = \frac{1}{2} \sum_{i,j} (e^2/4\pi\epsilon_0)(q_i q_j/d_{ij}) + (d_{ij}^{\text{min}}/d_{ij})^{12}. \quad (2)$$

The Coulomb interactions resulting from atomic charges q_i are calculated using the Ewald sum according to De Leeuw's method (De Leeuw *et al.*, 1980). d_{ij} is the distance between the two atoms i and j , and d_{ij}^{min} is a parameter indicating the minimum observed distance between the two atom types. These values may be readily obtained from the ICSD (Bergerhoff *et al.*, 1996; Brandenburg, 1989) or even common chemical knowledge, thus leading to a pronounced simple and transparent parametrization of the potential.

Alternatively, better potentials, like Buckingham or Lennard-Jones potentials, may be used in addition to the Coulomb interactions, provided that adequate potential parameters are available for the compound under investigation. Missing parameters can be obtained by fitting to known crystal structures of similar compounds using, *e.g.*, the well known crystal-lattice code *GULP* (Gale, 1993). A better and more accurate potential function makes the solution of the crystal structure easier for compounds for which only relatively raw diffraction data are available.

For most intermetallic compounds, a simple repulsion function parametrized with minimum interatomic distances d_{ij}^{min} can be employed for the purpose of structure solution. E_0 , containing the details of the attractive interaction of polarizable ion cores in an electron gas, is set equal to a constant ($= 0$):

$$E_{\text{pot}} = \frac{1}{2} \sum_{i,j} E_{ij}^{\text{rep}} + E_0, \quad (3)$$

$$E_{ij}^{\text{rep}} = \begin{cases} 0 & \text{if } d_{ij} \geq d_{ij}^{\text{min}} \\ (d_{ij}^{\text{min}}/d_{ij})^6 - 1 & \text{if } d_{ij} < d_{ij}^{\text{min}} \end{cases}. \quad (4)$$

This simple 'potential' may also be used as a 'penalty' type function prohibiting unphysically short atom-atom distances for any chemical system if no adequate potential is known, requiring, however, that a relatively high-quality diffraction pattern is available.

2.4. Comparison of experimental and calculated diffraction patterns

The following prescription for the calculation of the residual value R_B in equation (1) avoids the often ambiguous extraction of intensity values $I(hkl)$ from the experimental diffraction pattern:

$$R_B = 100 \sum_{2\theta} |I_{\text{exp}}(2\theta) - I_{\text{calc}}(2\theta)| / \sum_{2\theta} I_{\text{exp}}(2\theta). \quad (5)$$

The intensity values $I_{\text{exp}}(2\theta)$ may be readily calculated from a diffraction pattern of sufficient quality using standard powder diffraction software. Since it is assumed that the given unit cell corresponds to the Bragg angles 2θ in the peak-list file (possibly calculated from the unit cell after indexing), any remaining small deviations between the observed and the calculated 2θ values are balanced by assigning the observed intensity values I_{exp} to the next calculated Bragg peak position (2θ). Thus, the problem of an appreciable increase in the R_B value caused by deviations between the experimental and the calculated peak positions is avoided.

The first step for the evaluation of $I_{\text{calc}}(2\theta)$ is the calculation of intensities $I_{\text{calc}}(hkl)$ from the current atomic arrangement (configuration):

$$I_{\text{calc}}(hkl) = S L_p |F(hkl)|^2. \quad (6)$$

S is a scaling factor that is chosen in such a way that the sum of the intensities both of the calculated and of the measured diffraction pattern are equal. L_p is the common Lorentz-polarization factor which depends on the geometry of the diffractometer (Kasper & Lonsdale, 1959). For example, for Debye-Scherrer geometry

$$L_p = (1 + \cos^2 2\theta) / 2 \sin^2 \theta \cos \theta. \quad (7)$$

$F(hkl)$ is the structure factor for each possible Bragg reflection (hkl). The $F(hkl)$ are calculated from the given cell parameters and the fractional atomic coordinates (x_j, y_j, z_j) of all atoms j in the unit cell, *i.e.* no crystal symmetry other than translational symmetry is assumed (space group $P1$):

$$F(hkl) = \exp[-B \sin^2 \theta(hkl)/\lambda^2] \times \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)]. \quad (8)$$

As in most cases the overall atomic temperature factor B is unknown at the beginning of the optimization process, it should be adapted after each optimization step in order to achieve the best possible agreement between the calculated and the experimental powder pattern. λ is the wavelength of the X-ray (or neutron) radiation,

and f_j is the atomic form factor (or scattering length) of atom j .

The $I_{\text{calc}}(hkl)$ values obtained from equation (6) are subsequently transformed into $I_{\text{calc}}(2\theta)$. This is achieved by adding all those intensities $I_{\text{calc}}(hkl)$ for each of which the $2\theta(hkl)$ value lies in the interval $(2\theta - \Delta\theta, 2\theta + \Delta\theta)$:

$$I_{\text{calc}}(2\theta) = \sum_{hkl} J(hkl, 2\theta) \quad (9)$$

where

$$J(hkl, 2\theta) = \begin{cases} 0, & 2\theta(hkl) < 2\theta - \Delta\theta \\ I_{\text{calc}}(hkl), & 2\theta - \Delta\theta \leq 2\theta(hkl) \leq 2\theta + \Delta\theta \\ 0, & 2\theta(hkl) > 2\theta + \Delta\theta \end{cases} \quad (10)$$

$\Delta\theta$ corresponds to the resolution of the diffractometer in 2θ ; in our test cases we assumed a rather low value of $\Delta\theta = 0.01$. This value is more or less typical for good synchrotron measurements and rather low for conventional laboratory X-ray diffraction equipment. However, the choice of this value proved to be not overly critical: minor changes have generally no significant influence on the results of most calculations.

3. Implementation and testing

3.1. Implementation

The method described in the preceding section was implemented in our program *Endeavour*. It consists of a Windows[®]-based graphical user interface and a separate program (*Endeavour-kernel*) that actually performs the calculation and may be run on any workstation or PC. In the following a more detailed description of structure determination from raw powder diffraction data employing *Endeavour* is given.

The first step when beginning with the raw data set obtained from the diffractometer is to locate the peaks and extract their intensities as a function of the diffraction angle 2θ . Afterwards, this peak list is submitted to an indexing program [e.g. *ITO* (Visser, 1969), *TREOR* (Werner *et al.*, 1985) or *DICVOL* (Boultif & Louer, 1991)] in order to obtain the unit-cell parameters. The number of formula units per unit cell is then calculated from Biltz space increments (Biltz, 1934) or atomic radii.

These preliminary steps are definitely necessary when new crystal structures have to be solved; however, we omitted them in most cases, because all test structures for our method were previously known.

The input to our program (presuming that appropriate minimum interatomic distances or potential parameters are already present in the program's database) consists of the peak list (intensity *versus* 2θ for all observed reflections), the composition and the number of formula units per unit cell, and a keyword concerning the 'chemistry' of the compound, *i.e.* whether it may be

roughly described as an ionic or metallic compound. This keyword is used by the program in order to set some standard parameter settings, reducing the necessary input to an absolute minimum in general. However, all parameters may be set independently if necessary. The optimization may last between a few minutes for small structures, like rutile, to a couple of days for large unit cells containing many dozens of independent atoms.

Subsequently, the symmetries and the space group of the output structural model can be determined using the programs *SFND* (Hundt *et al.*, 1999) and *RGS* (Hannemann *et al.*, 1998), respectively. Finally, the model may be submitted to a Rietveld refinement yielding the crystal structure.

3.2. Testing

Following this prescription, *Endeavour* has been successfully tested on a large variety of crystalline ionic and intermetallic compounds (Table 1). The starting configurations were generated by random distribution of the atoms within the unit cell. Afterwards, simulated annealing steps were performed until the control parameter K was reduced from initially 100.0 to 10^{-5} . The so-called 'temperature program' recalculated the control parameter after m steps:

$$K_{i+1} = 0.9 K_i. \quad (11)$$

The number of steps m for each control parameter value depended on the acceptance rate of the preceding steps: if the acceptance rate was above the optimum value ($\sim 40\%$), $3n$ steps were performed; if the rate was lower than the optimum value, the interval between two modifications of the control parameter was $9n$ steps; if the acceptance rate was near the optimum, $300n$ steps were performed for each control parameter value. In all cases, n denotes to the number of atoms in the unit cell.

Each step was chosen at random, according to the following move class: (i) displacement of a randomly chosen atom in a randomly chosen direction (maximum width 0.25 Å) (95%); (ii) exchange of two randomly chosen atoms, followed by a local optimization for $10n$ steps (n = number of atoms in the unit cell) (5%).

Calculations have in most cases been performed on experimental diffraction data provided as peak lists in the Powder Diffraction File (PDF2) database from the International Centre for Diffraction Data (ICDD). In those cases where no experimental diffraction data were available, diffraction patterns have been calculated from crystallographic data obtained from the ICSD (Bergerhoff *et al.*, 1983) using *LazyPulverix* (Yvon *et al.*, 1977). The final Rietveld step mentioned above has been omitted from our test scheme since no raw diffraction data suitable for Rietveld refinement were available for most of the compounds under investigation.

Concerning the potential function, the simple potential given in equation (2) was employed for all ionic test

Table 1. *Test compounds whose crystal structures have been successfully 'determined' from powder data*

The powder-data source is either given as the PDF index number (International Centre for Diffraction Data) or as a reference; entries marked *Lazy* have been calculated using *LazyPulverix* (Yvon *et al.*, 1977).

Compound	'Chemistry'	Atoms/cell	Powder data	Source
Na ₃ PS ₄	Ionic	16	Experimental	Henseler (1991)
CaCO ₃ (calcite)	Ionic	30	Experimental	47-1743
CaCO ₃ (aragonite)	Ionic	20	Calculated	<i>Lazy</i>
MgSiO ₃ (enstatite)	Ionic	80	Calculated	<i>Lazy</i>
Mg ₂ SiO ₄ (forsterite)	Ionic	28	Experimental	34-0189
Na ₃ OCl	Ionic	5	Calculated	<i>Lazy</i>
Na ₃ OBr	Ionic	5	Calculated	Haas (1998)
Al ₂ O ₃ (corundum)	Ionic	30	Experimental	46-1212
SiO ₂ (quartz)	Ionic	9	Experimental	46-1045
SiO ₂ (cristobalite)	Ionic	12	Experimental	39-1425
SiO ₂ (stishovite)	Ionic	6	Experimental	45-1374
TiO ₂ (rutile)	Ionic	6	Experimental	21-1276
TiO ₂ (anatase)	Ionic	12	Experimental	21-1272
TiO ₂ (brookite)	Ionic	24	Experimental	29-1360
MgO	Ionic	8	Experimental	45-0946
MgF ₂	Ionic	6	Experimental	41-1443
CaF ₂	Ionic	12	Experimental	35-0816
In ₂ Ni ₂₁ B ₆	Metallic	116	Experimental	Adelsberger (1998)
In ₂ Ni ₆ B	Metallic	36	Experimental	Adelsberger (1998)
MgCu ₂	Metallic	24	Calculated	<i>Lazy</i>
MgZn ₂	Metallic	12	Experimental	34-0457

structures, and the repulsion function [equation (3)] for all intermetallic compounds (Table 1). They were parametrized by minimum distances between each pair of atom types deduced from the ICSD (Bergerhoff *et al.*, 1983; Brandenburg, 1989).

For our test structures, a correct solution was assumed if (a) a sufficiently low R_B value was achieved [$\leq 10\%$; in a few cases (low-quality diffraction data) up to 26%], (b) the final configuration also corresponded to a minimum of the potential energy, (c) the space group of the final configuration determined by RGS was identical to that of the correct crystal structure, and (d) the atomic arrangement of the final configuration could not be distinguished visually from the correct structure using the visualization program *Diamond* (Bergerhoff *et al.*, 1996). All calculations were performed on a Intel-PII CPU (400 MHz) running Linux 2.0.29. While generally a more or less large number of runs using different random number sequences has to be performed when dealing with simulated annealing because of the limited calculation time (Schön & Jansen, 1995), it turned out that this was generally not necessary in our case. For each example in Table 1, the first run yielded the correct crystal structure. A more detailed investigation using randomly selected test cases showed that in most cases 10/10 runs yielded the correct structure. Only when diffraction data of low quality had to be employed (*e.g.* Na₃PS₄), was the success rate reduced.

Recently, the program has been applied to the compound Na₃PO₃S, the structure of which is not known. So far, no single crystals have been obtained, and the structure could not be solved from X-ray powder diffraction data by conventional techniques.

However, *Endeavour* calculated a very good structure candidate from the powder data, which is in good agreement with neutron diffraction data (Pompetzki & Jansen, 1999). Further investigations are currently in progress.

4. Discussion

Up to now, in the literature there have been few reports containing a similar prescription (Deem & Newsam, 1992; Falcioni & Deem, 1999), all of them being dedicated to a single chemical system (zeolites). Our concept of a Pareto optimization of diffraction data and potential energy goes beyond this earlier work, aiming for a merging of the methods used in structure prediction and structure solution. In fact, the combination of structure prediction and powder diffraction analysis has both synergetic and complementary aspects, depending on the particular problem. If both an accurate potential function and a high-quality powder diffraction pattern are available, the optimization is very fast and yields the correct crystal structure with high probability. However, if only a very approximate potential is available, this can be compensated for to a large degree by a high precision powder diffraction diagram. One might then use the potential only for ensuring reasonable distances between the various atom types, thus enforcing the optimization according to the difference in powder diffraction patterns. If, on the other hand, only few and not very reliable diffraction data are available for the compound under investigation, a high-quality potential can nevertheless lead to reasonable structures. Here, the effect of the R_B term lies in the enhancement of one of

the many structures that constitute local minima of the potential energy.

One should note that our method can also be of use in cases where a high crystal symmetry leads to very few diffraction peaks and thus to few parameters, limiting the complexity of the atomic arrangement that can be solved by conventional methods. The additional information contained in the potential can help to solve even complex highly symmetric crystal structures from their powder diffraction patterns.

Although the determination of the space group from the systematic absences of certain reflections in the indexed powder diffraction pattern is often not overly difficult when dealing with crystals of organic molecules, this is frequently not the case when the structures of complex inorganic compounds have to be solved. Since our concept is based on triclinic crystal symmetry (space group *P*1), there is no need to provide any space-group information in the input of the calculation.[†]

Our experience has shown, however, that certain basic requirements have to be fulfilled for a successful application of our method. Firstly, the quality of the powder pattern has to be high enough so that enough accurate peak positions are available to allow a reliable indexation resulting in the correct unit cell. Secondly, the peaks should not be too broad, in order to allow the extraction of fairly accurate intensities at the peak positions. Additionally, the content of the unit cell should be known accurately; otherwise the global optimization will take several orders of magnitude longer, since we would have to vary the number of atoms in the unit cell in addition. This touches on the problem of partial occupation of sites, which is currently being investigated. Finally, the approximate description of the structure of the compound under investigation must be possible using a simple empirically parametrized potential, *i.e.* the desired structure should exhibit a low potential energy, preferably constituting a deep minimum of the energy landscape.

If these conditions are not fulfilled, we have found that in some cases a diffraction pattern or potential of very poor quality can block the optimization process. However, we expect that improvements in both the quality of powder diffraction data and the accuracy of the energy functions available for global optimization will make more problems amenable to solution.

One argument frequently raised in the context of direct-space methods is their need for a large amount of computing time, which increases rapidly with the complexity of the crystal structure under investigation. For example, the solution of a crystal structure containing some hundred degrees of freedom (*e.g.* $\text{In}_2\text{Ni}_{21}\text{B}_6$, *cf.* Table 1) may even take a few weeks on a

Pentium[™] II processor with a clock speed of 400 MHz. However, we believe that this issue is becoming less relevant by the increasing availability of very cheap and fast personal computers.

Though a variety of more sophisticated Monte Carlo optimization techniques has been developed (Falcioni & Deem, 1999), our results show that even the standard simulated annealing algorithm is capable of solving crystal structures from powder diffraction data with a very high degree of probability, provided that a properly chosen move class and 'temperature program' are employed.

Despite the limitations mentioned above, we believe that the approach presented in this paper will allow the solution of many crystal structures not possible with the methods available up to now.[‡]

A variety of features not mentioned in this paper are currently being investigated, including the ability to solve crystal structures for molecular compounds through the implementation of a valence force field, and the possibility to preset a minimum of required symmetry elements, thus narrowing the available configuration space, leading to an increase in calculation speed.

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[†] Of course, once the structure is known in *P*1, applying *SFND* (Hundt *et al.*, 1999) and *RGS* (Hannemann *et al.*, 1998) will yield the full space group.

[‡] The corresponding program *Endeavour*, capable of running on a large variety of platforms including PCs and common workstations, is available from Crystal Impact GbR (1999).

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