Inorganic Materials

Cerny, Radovan

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Radovan Černý
Laboratory of Crystallography, University of Geneva, Switzerland

Ab initio structure determination - polyhedral description

Inorganic compounds usually do not contain isolated molecules. This does not mean a particular difficulty for the *ab initio* structure solution methods working entirely in the reciprocal space (RSM). However, it becomes a difficulty for the methods working entirely (global optimization methods) in the direct space (DSM) and using the chemical knowledge in this space (for a comprehensive review on the methods see [1]). The structure solution algorithm working in the direct space has to know how to define basic structural blocks of the crystal which are then manipulated (optimized) by the algorithm.

The choice of the structural blocks is easy when isolated molecules are present in the crystal like in organic or coordination compounds where the molecules are easily described by a finite number of the internal molecular coordinates (bonding distances, angles and dihedral angles). A molecule is naturally an isolated structural block that can be moved in the unit cell, and deformed from its planar form. No sharing of atoms between the molecules occurs. The situation becomes rather unclear when one tries to model the crystal structure of a non-molecular compound. The definition of a finite structural block for a crystal like iron or sodium chloride is not unambiguous; should it be one atom, first coordination sphere of each atom, structural sheet of finite thickness, the asymmetric unit?

Coordination polyhedra, typically the first coordination spheres, of selected atoms, which will generate the whole inorganic crystal structure, can always be identified. These polyhedra will share corners, edges or faces. A wide range of polyhedra can be defined, and these are naturally described using again bond distances, angles and dihedral angles. Sharing of atoms between the polyhedra is either evident (for example exclusive corner sharing of SiO_4 tetrahedra in alumino-silicates [2]), or can be better described generally with an automatic, adaptive routine, the Dynamical Occupancy Correction (DOC) which handles also the special Wyckoff positions as it is used in the program Fox [3]. The optimization algorithm of DSM must be able to move smoothly the building blocks to the positions when they share atoms or to move an atom on the special position, while also allowing separation of the building blocks or moving the atom *away* from the special position, without *any* intervention from the user.

The polyhedra are typically described using Z-matrices as for the molecules [3]. The restraint-based description [4] of the polyhedra then solved some pitfalls of Z-matrices, however, with less benefit for the non-molecular compounds. A careful choice of the structural blocks may significantly improve the convergence of the DSM as illustrated on the example of AlMePO-γ phosponate [5] where the modelling by two free Al atoms converges faster than the modelling by AlO_4 tetrahedron and AlO_5 trigonal bipyramid.

Direct- or Reciprocal- space method?

The principal difference between DSM and RSM and an advantage of the former is that DSM does not require the extraction of integrated intensities of individual reflections which are needed for RSM. In the case of powder patterns of inorganic compounds showing often broad peaks, because of particular sample synthesis like mechanochemistry (ball-milling) or in situ studies of phase transformations and non ambient studies the DSM are the only option as no reliable integrated intensities can be extracted.

An excellent example that has been solved *ab initio* by both DSM and RSM, and shows effectiveness of both approaches when well crystallized samples are available, is $Mg(BH_4)_2$ (Fig. 1). With 55 atoms in the asymmetric unit it represents one of the most complex atomic arrangements ever solved from powder diffraction data. The correct structure was found independently by DSM [6] and by RSM [7]. In both cases high resolution synchrotron data were required for indexing. In the DSM approach, the structure was modelled by five free Mg atoms and ten rigid tetrahedral BD_4 groups, and optimized jointly with synchrotron and neutron data by using the program Fox [3]. The correct structure was recognized after several hours of optimization (guidelines for efficient use of Fox can be found in [8]). In the RSM approach, the structure was solved with the aid of the program EXPO [9] using only synchrotron data. The positions of Mg and B atoms were recognized in electron density maps. In both cases the structure was refined by Rietveld refinement keeping the borohydride groups rigid.

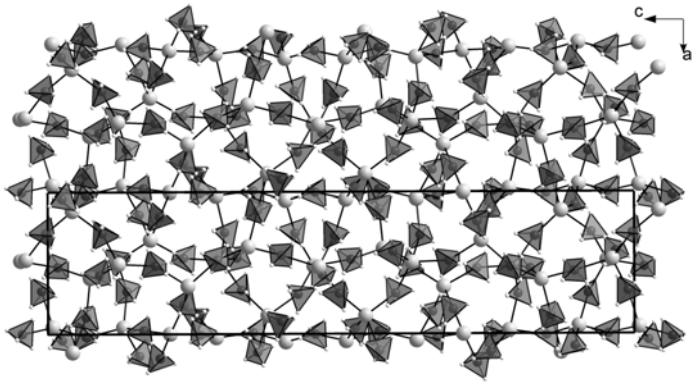

Fig.1. Structure of $Mg(BH_4)_2$ viewed along the hexagonal *b* axis, showing two unit cells. Dark grey (partially transparent) tetrahedra are BH_4 units; Mg atoms in light grey.

Need for accurate unit cell content

Knowledge of the chemical composition and estimation of the unit cell content are the necessary information for most structure solution algorithms. The DSM may successfully work with overestimated cell content as the DOC can simply merge excess atoms (but does not create missing atoms!).

The recently discovered borohydrides $AZn_2(BH_4)_5$ (*A*=Li, Na) [10] are an example how important is the correct estimation of the unit cell content for an unknown phase. In a parallel study [11] the chemical composition of the ball milled product was wrongly estimated as $AZn(BH_4)_3$, and led to structural models that have shortcomings in Rietveld plots (Fig. 2.) which are not easily detectable from the powder diffraction data. Such a structural model can have balanced interatomic forces as shown by the DFT optimization, but does not correspond to a stable polymorph at given conditions.

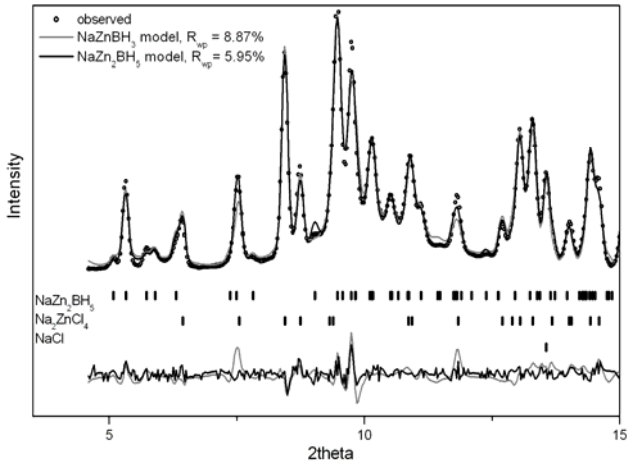

Fig.2. Comparison of Rietveld plots for wrong, $NaZn(BH_4)_3$, and correct, $NaZn_2(BH_4)_5$, structural models, both in the same monoclinic cell (s.g. $P2_1/c$, *a*=9.440(4), *b*=16.573(4), *c* =9.110(2) Å, β=112.99(3) °).

Only warning about the wrong structural model came from the significant increase of the cell volume (+5.2 %) in the DFT optimized structure, because of higher cell content (16 cations and 24 anions) compared to the correct model (12 cations and 20 anions). It means also that the wrong model is more packed (34.52 $Å^3$/ion) than the correct one (40.81 $Å^3$/ion) as calculated on DFT optimized cells. Another warning about the wrong model could have been certainly obtained from the measured density, a difficult experiment for a relatively reactive powder. In the case of multiphase samples containing new phase with unknown exact chemical composition it is therefore crucial to perform the synthesis of starting mixtures in several different ratios of the starting compounds. This procedure allows deducing the chemical composition of the new phase from molar fractions of known phases in different mixtures.

Structure validation and verification

A post-experimental DFT-optimization helps to validate new structures, locate light atoms (hydrogen), especially when using high-pressure diffraction data [12], and even correct the symmetry and some structural details as shown on following examples:

The difficulty in finding the correct orientation of BH_4 tetrahedra led to the overlooked 2-fold axes in the $Mg(BH_4)_2$ space group symmetry originally identified as $P6_1$ [6, 7]. The DFT optimization of the structural model [13] has suggested the true symmetry as $P6_122$, which was then unambiguously confirmed by the single crystal X-ray diffraction [14]. The fact that the structural solution has been found independently by DSM and RSM in the lower Laue symmetry 6/*m* of the space groups $P6_1$ rather than in the true Laue symmetry 6/*mmm* of the true space groups $P6_122$ can be also understood by more degree of freedom (*hkl* and *khl* are independent) in 6/*m* allowing to correct the systematic errors of the powder diffraction data (grain statistics) having the symmetry 6/*mmm*.

In the case of $Li_4Al_3(BH_4)_{13}$ (*P*-43*n*) the DFT optimization [15] of the experimental structure has corrected the orientation of the complex anion $[Al(BH_4)_4]^-$ and modified so the bonding scheme in the structure from isolated complex ions $[(BH_4)Li_4]^{3+}$ and $[Al(BH_4)_4]^-$ rather to a 3D-framework structure (Fig. 3). The corrected model was indeed confirmed by the Rietveld refinement. A similar situation occurred for a nanocrystalline inorganic-organic hybrid compound $VO(C_6H_5COO)_2$ [16] where the correct orientation of the VO_6 octahedron was revealed by the DFT calculation.

The post-experimental DFT-optimization of the crystal structures allows achieving the global minimum in the Rietveld refinement which is not easily visible from the diffraction data only, and can be thus highly recommended.

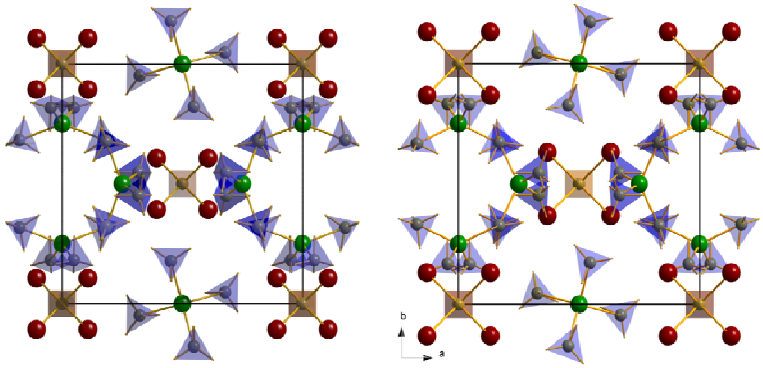

Fig.3. Unit cell of $Al_3Li_4(BH_4)_{13}$ as solved from SR-XPD (left) and as corrected by DFT optimization (right). Complex cation $[(BH_4)Li_4]^{3+}$ centred by BH_4 tetrahedron in brown (light grey), complex anion $[Al(BH_4)_4]^-$ centred by Al atom in green (dark grey).

Symmetry guided refinement, phase transitions

The analysis of crystal symmetry plays an important role in the structure solution/refinement of inorganic compounds. The most complex inorganic structures were solved from powder diffraction data by the symmetry analysis of superstructures based on a well described average structure. Good example is α-$Bi_2Sn_2O_7$, a 176 atom crystal structure based on a pyrochlore structure [17]. Other example of symmetry guided refinement is the parametric Rietveld refinement [18], *i.e.* constraining the crystallographic parameters by set of equations which may have a physical basis, and follow the crystal symmetry. Structural phase transitions are one of the examples [19].

Multiphase samples, impurities

Solid state route synthesis is a method often used for the preparation of inorganic compounds. The resulting products may contain more than one phase like unreacted starting components and side reactions products. As the bottle-neck of the *ab initio* structural studies is still indexing of the powder data, multiphase samples introduce an additional complication.

A successful strategy consists of the so-called 'decomposition-aided indexing', which utilizes *in situ* diffraction as a function of the temperature (*T*-ramping) up to the decomposition/melting temperature of different phases. This procedure allows to separate diffraction peaks of individual phases as illustrated in Fig. 4 by synchrotron powder diffraction data for a ball milled KBH_4-$ScCl_3$ mixture [20].

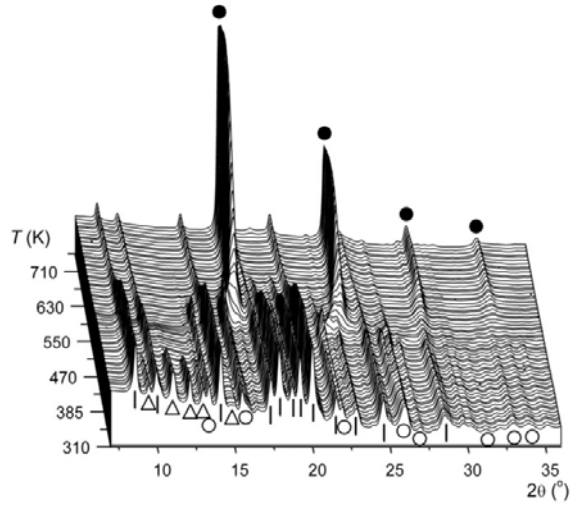

Fig.4. *In situ* synchrotron radiation X-ray powder diffraction data for a ball milled sample of KBH_4-$ScCl_3$ (2:1) (*RT* to 580 K, $\Delta T/\Delta t$ = 5 K/min, λ = 0.9707 Å). Only utilization of T-ramping allowed for determination of attribution of observed peaks to individual phases, $KSc(BH_4)_4$ and K_3ScCl_6, and led to a successful indexing of the RT-powder pattern. Symbols: Δ $KSc(BH_4)_4$, | K_3ScCl_6, O KBH_4 and ● KCl.

The T-ramps (as well as any set of powder patterns collected as a function of external stimuli like pressure, excitation by a light) play an important role in the analysis of multiphase samples, as already mentioned. The studies of physical properties (thermal dilatation, compressibility), and of phase transitions are of course the original reason of the non-ambient diffraction studies.

Weak superstructures and lattice pseudo-symmetry

The arrangement of atoms in the lattice of an inorganic compound may show a small deviation from an arrangement with higher symmetry or shorter periodicity. A typical example are metal hydrides where this deviation is created by positioning H atoms in the matrix of metal atoms which becomes then only slightly deformed or by positioning a lower symmetry structural block like BH_4 tetrahedron on a high symmetry Wyckoff site. Because of a small deformation of the metal matrix and the low scattering power of hydrogen for X-rays, the splitting of peaks caused by lowering the symmetry is not very strong and the superstructures peaks are very weak in X-ray patterns as was the case of $Mg_6Co_2H_{11}$ [21] or $Y(BH_4)_3$ [22,23].

Chemical and positional disorder - local structures

Chemical disorder is often observed in metal alloys where metal sites may have mixed occupation. When the occupation of individual sites by different metals is not statistically random, it can be analyzed provided the scattering contrast between the metals is strong enough. It can be achieved either using the X-ray and neutron data jointly or by resonant X-ray scattering. Note that for the case of *n* atomic species (including vacancies) on one Wyckoff site, one needs *n*-1 diffraction patterns with

different contrast between the scatterers under the question. An example of the analysis of the multi-substituted $LaNi_5$ alloy is given in [24].
Positional atomic disorder may show a local order (short range order) which can be studied from the diffuse intensity of the scattered radiation. The diffuse scattering from polycrystalline samples may be studied by using the Pair Distribution Function (see [25] for more details) like local hydrogen ordering in Laves phases [26].

Powder vs. Single crystal

Independent studies of the orthorhombic (*Cmca*) $Mg_{1+x}Ir_{1-x}$ by single-crystal and powder diffraction methods [27] have allowed a comparison of the structural results obtained by two different methods on a compound having rather a complex crystal structure with 304 atoms in the unit cell. The investigated volume in the reciprocal space was approximately the same in both experiments, but with more than 4000 unique reflections and redundancy factor of 7 for single crystal experiment and 754 unique non-overlapped reflections for the powder data. The atomic positional parameters from both methods are identical within 3-4 times standard uncertainties (s.u.) of the powder diffraction with the s.u. of the powder diffraction by one order of magnitude higher than corresponding s.u. of single crystal results. On the contrary the s.u. of the lattice parameters were by more than one order lower in favour of the powder diffraction.
It is sometimes possible to find a single grain of sufficient size for X-ray single crystal diffraction in an apparently powder sample, as was the case for $Li_4BN_3H_{10}$ [28] or $LiBH_4$ [29]. Even a multi-domain single crystal obtained by a low temperature annealing of an air- and moisture-sensitive $Mg(BH_4)_2$ has produced more accurate structural results than powder diffraction [14].

Conclusions

The powder diffraction on inorganic compounds is not a routine work. A crystallographer has to face numerous crystallographic challenges: complex structures, superstructures, pseudo-symmetries, twinning, chemical and positional disorder, local order, and structural solution from low quality data. On the other hand many powerful tools are available: resonant scattering, total scattering analysis, fast in-situ data collection. The good knowledge of basic crystallographic concepts like symmetry analysis, theory of scattering including diffuse effects, aperiodic crystals, and knowledge of limits and accuracy of powder data helps to avoid erroneous conclusions. The final cut should be always left to the crystal chemistry analysis.

Acknowledgments

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