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Solving crystal structures of metal and chemical hydrides

Radovan Černý*

Laboratoire de Cristallographie, Université de Genève, 24, quai Ernest-Ansermet, 1211 Genève 4, Switzerland

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Abstract. The methods of structural characterization of metal and chemical hydrides are reviewed. The existing difficulties and problems are outlined and possible solutions presented. It is shown that powder diffraction, and especially the Direct Space Method, is essential component of hydride research. Crystal structures containing as many as 55 independent atoms (including hydrogen) have been fully characterized using powder diffraction. This is of great importance, because rapid collection of powder data thanks to modern synchrotron and neutron time-of-flight sources opens the possibility for fast *in-situ* studies, mapping of phase transitions induced by the temperature, pressure, hydrogen content, and chemical reactions. The progress in structural characterization of hydrides goes hand in hand with the progress in the powder diffraction methodology.

Introduction

The study of hydrides needs precise crystal structure information. It can be obtained by radiation scattering experiments (X-rays, neutrons, electrons) using elastic and coherent scattering (Bragg scattering) on the periodic lattice of a crystal (c.f. [Giacovazzo (2002)]). Hydrogen is a very weak scatterer of X-rays compared to metal atoms as the atomic scattering power for X-rays is directly proportional to the atomic number. Scattering experiments on hydrides therefore need neutron radiation (for exceptions see below) and deuterated samples. Coherent neutron scattering length of hydrogen (−3.74 fm) and deuterium (6.67 fm) is then comparable to that of metals. Deuterium is also preferred to avoid high incoherent scattering length of hydrogen which introduces a high background in the diffraction patterns. Neutron scattering experiments generally provide values of interatomic distances with higher precision due to the constancy of the coherent scattering length with the momentum transfer ($Q = 2\pi/d$, d – inter-planar spacing) compared to X-rays where the atomic scattering power decreases substantially as a function of Q. Scattering experiments can be performed on a single crystal or polycrystalline (powder) sample. Single crystals provide typically structural results with a precision that is one order of magnitude better than powder samples.

To our best knowledge the first structural characterization of a metal hydride using a diffraction method is the work of J. M. Bijvoet and A. Karssen in their doctoral thesis in Amsterdam [Bijvoet and Karssen (1922)]. Inspired by Bragg's results and using the X-ray powder diffraction (XPD) they have determined that LiH is isostructural with NaCl. Neutron powder diffraction (NPD) at Oak Ridge National Laboratory was for the first time used to solve the structure of NaH and NaD [Shull *et al.* (1948)], which are again isostructural to NaCl. These relatively simple compounds were also used to determine the neutron scattering lengths of sodium, hydrogen and deuterium. If we do not consider the report on the crystal structure of $LiBH_4$ [Harris and Meibohm (1947)], because no atomic coordinates were given, then the first hydride structure determination from X-ray single crystal diffraction (XSD) is that of [Juza and Opp (1951)] on $LiNH_2$ and Li_2NH. The first metal hydride structure determination using neutron single crystal diffraction (NSD) was done on K_2ReH_9 [Abrahams, Ginsberg and Knox (1964)].

The structural characterization of hydrides is faced with several substantial difficulties such as the low X-ray scattering power of hydrogen, and the lack of single crystals. We will therefore principally discuss the powder diffraction (PD) experiments. Furthermore the crystallographers analyzing the hydrides face many different crystallographic challenges that include: complex structures, superstructures, pseudo-symmetries, twinning, chemical and positional disorder, structural solution from low quality data (powder patterns), joint use of several data sets, resonant scattering, fast *in-situ* data collection etc. In this structure determination review we will discuss the important progress achieved in structural characterization of hydrides over the last 15 years, alongside the progress in powder diffraction methodology.

In this review we will consider both metal hydride, the compounds of metals and hydrogen, and chemical hydrides that include borohydrides, alanates, amides, imides. We do not review molecular compounds, which are typically coordination compounds, but will concentrate on compounds that do not contain easily recognizable isolated molecular units. These compounds are sometimes called extended solids or non-molecular compounds. We

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* e-mail: Radovan.Cerny@unige.ch

will use the term hydrogen and hydride without regarding the isotopic purity, *i.e.* for hydrogen and deuterium, unless specified.

Single crystal diffraction

Single crystal diffraction is not often used in hydride research due to the solid state route synthesis that does not favor the crystal growth. Isolated examples do exist such as the orthorhombic structure of BaH_2 which has been refined from XSD data collected on a laboratory source [Snyder, Borrmann and Simon (1994)]. Despite the strong scattering of barium ($Z = 56$), two hydrogen sites were successfully located in electron density maps and their coordinates refined to values which give the same Ba—H distances within the precision limits as the NPD experiment [Bronger, Chi-Chien and Müller (1987)]. The uncertainties of these results are, however, by an order of magnitude bigger from the X-ray than from the neutron experiment. An interesting comparison is proposed with the XSD work on $KNaReH_9$ [Stetson and Yvon (1995)] where no hydrogen atoms were located in the electron density maps. Both compounds crystallize in the same space group (*Pnma*), the coordination of Ba and Re (located both on the same Wyckoff site 4*c*) by hydrogen is the same (tricapped trigonal prism), both crystals were of similar size ($\sim$0.001 mm^3), and even the same type of diffractometer was used (CAD4). However, the scattering from rhenium is even stronger ($Z = 75$), and hydrogen is located in $KNaReH_9$ (as proposed, but not refined) on six Wyckoff sites compared to only two in BaH_2. The limit of the XSD experiment on metal hydrides with laboratory sources is somewhere between these two compounds.

XSD on both a metal alloy and its hydride using the same crystal were performed on $LaNi_3BH_x$ ($x = 2.5–3.0$) [Filinchuk and Yvon (2005a)]. A single crystal was extracted from the $LaNi_3B$ alloy, mounted on a glass fiber, and measured on a Stoe IPDS II diffractometer equipped with an image plate detector and Mo X-ray tube. The crystal structure was solved and refined in the orthorhombic space group *Imma*. After data collection, the alloy crystal was removed from the diffractometer and, while still on the glass fiber, hydrogenated in an autoclave. Microscopic examination showed that the crystal had cracked upon hydrogenation, but a fraction of $\sim$40% was still present on the glass fiber. Data were collected on the same diffractometer with conditions optimized for lower quality single crystal. During data collection (35 h), the cell volume decreased smoothly by $\sim$0.6% suggesting some hydrogen desorption; this was accounted for during intensity integration. Two randomly twinned domains of comparable scattering power were identified, and the reflections of only one were used for the structure solution and refinement of the hydride structure in the space groups *Cmcm*. The hydride scattering data were of lower quality ($R_{\mathrm{int}} = 0.11$) than that of the alloy ($R_{\mathrm{int}} = 0.03$), and consequently all *R*-factors were higher for the hydride. However, the data allows complete characterization of metal lattice of the hydride (GoF = 1.15 in both cases). Four hydrogen atoms were then localized in a powder sample by NPD.

The work on K_2ReH_9 [Abrahams, Ginsberg and Knox (1964)] still remains as one of the rare structural characterization of metal hydrides by NSD. The key problem is the growth of single crystals with a sufficient size to allow NSD experiment. The crystals of K_2ReH_9 were of the volume of 26.8 and 10.1 mm^3, and two crystals were used for the data collection, first to collect the zone *hk*0 and the second to collect the zone *h*0*l*. The structure was then solved and refined within these two projections. The hydrogen atoms were localized in the neutron scattering power density projections and refined anisotropically. Latest developments of the NSD instrumentation, especially Laue techniques like VIVALDI at the ILL Grenoble (*www.ill.eu*) and SXD at the ISIS spallation neutron source (*www.isis.rl.ac.uk*), allow a fast collection of full data sets.

Powder diffraction

A general review of structure determination from powder diffraction (SDPD) can be found in [David and Shankland (2008)] and [David *et al.* (2002)]. The method can be divided into two groups according to the working space: *Reciprocal space methods* (RSM), involving procedures developed for single crystal data like Direct or Patterson method, and optimized for powder data; *Direct space methods* (DSM), involving search in the direct space containing structural building blocks (free atoms, coordination polyhedra, molecules etc.), and an agreement factor between the observed and calculated powder diffraction data is evaluated, while the structural model is globally optimized to improve the agreement.

SDPD of hydrides can be divided on the time scale into three periods: In the early days (till 1969) the trial-and-error methods and application of Direct and Patterson techniques to the integrated intensities extracted from the analogous records of powder patterns were the typical approach and a good example is α-AlH_3 [Turley and Rinn (1969)]. In the second period the introduction of Rietveld method [Rietveld (1969)], a whole-pattern-fitting procedure, has allowed the refinement against powder data of structural models constructed from crystal-chemistry analysis. Typically, deuterium atoms were located from neutron data by refinement of occupancies of the available interstitial positions (*e.g.* $Zr_3V_3OD_x$ [Rotella *et al.* (1983)]) or of the positions predicted from electronic factors like for complex hydrides such as Mg_2FeH_6 [Didisheim *et al.* (1984)]. In 1992 the Rietveld method has evolved into DSM (the third period of SDPD) in the work [Newsam, Deem and Freeman (1992)]; for more detailed information see [Černý and Favre-Nicolin (2007)].

Although non-molecular materials generally have simpler chemical formulae than molecular compounds, they are often more complicated to solve from powder data. Perhaps the principal reason is the more complex topological possibilities of crystal structure compared to the molecular crystals containing well defined and isolated molecules. Metal hydrides often consist of connected polyhedra with *a priori* unknown topology of the connectivity. It complicates the interpretation of electron or nuclear scattering power density maps in RSM and the parametrization of the structural model for DSM. The practical "invisibility" of hydrogen for X-rays helps to split the SDPD procedure into two steps and to decrease the number of free parameters to be determined *ab initio*: The metal atoms sub-structure is solved from X-ray or synchrotron data, and then the deuterium positions are located from neutron data.

Indexing and space group determination

An essential first step in SDPD is unit-cell determination (indexing). With high resolution data (synchrotron), indexing is often straightforward. However, with poorer data and multiphase samples (often the case of hydrides), indexing can become a serious bottleneck. When the hydrogen contribution to X-ray scattering is practically invisible then indexing may provide only a subcell or a pseudocell, which on the other side is a simpler task for the indexing algorithm. The true cell is only found after analysis of the neutron data (see below). Useful guidelines for successful indexing can be found in [David and Shankland (2008)] and [Černý and Favre-Nicolin (2007)].

"Space groups are determined by examining diffraction patterns for systematically absent reflections. Determining absences for long *d*-spacing reflections is normally straightforward, but at shorter *d*-spacings reflection overlap in the powder pattern makes it a much more subjective process. While observing lattice-centering extinctions is usually relatively easy, the determination of the correct space-group-symmetry elements is generally more challenging" [David and Shankland (2008)]. This is even more valid for poorly crystallized hydrides with broad peaks and strong pseudosymmetry which is difficult to detect in the X-ray pattern due to weak X-ray scattering power of hydrogen. Probabilistic approaches to space-group determination have been developed that remove the need for subjective judgments about the presence or absence of classes of reflections throughout the pattern [Markvardsen *et al.* (2001)].

The determination of the space group is theoretically not necessary, as the structure can be searched in space group *P*1, however as the number of trials required to find the true solution increases exponentially with the number of independent atoms, a factor 2, 4, 8 up to 192 reduction in the number of atoms cannot be passed on. In the extreme case, like nanoparticles of hydrides, when no unit cell or space group candidate can be obtained, it is still possible to do a direct space determination using the Pair Distribution Function (PDF) modelling [Juháš *et al.*, 2006]. This analysis does not require long-range periodicity and symmetry (but does not exclude it), and is sensitive to the short-range (local) order [Egami and Billinge, 2003].

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. The decomposition of overlapping peaks in a powder pattern due to the projection of three-dimensional reciprocal space on one dimension (a radial distance from the origin) is a key problem of PD, and becomes very difficult in the case of badly crystallized samples and consequently broad diffraction peaks. Significant progress in the decomposition of overlapping peaks was achieved by employing an additional parameter like temperature (anisotropic thermal expansion) or preferred orientation when collecting the powder data (see [David and Shankland (2008)] for more details). RSM, however, still remains the most general powder diffraction tool. Application of new ideas such as the Charge Flipping Algorithm [Baerlocher *et al.* (2007)] allows the *ab initio* solution of any type of crystals including the modulated structures and quasicrystals without *a priori* knowledge of the crystal symmetry and composition.

An excellent example that has been tackled by both DSM and RSM and shows effectiveness of both approaches is $Mg(BH_4)_2$ (Fig. 1). It represents one of the most complex atom arrangements ever solved from powder diffraction data. It was solved ($a = 10.3182$, $c = 36.9983$ Å, space group $P6_1$) independently by DSM [Černý *et al.* (2007)] and by RSM [Her *et al.* (2007)]. In both cases high resolution synchrotron data were required

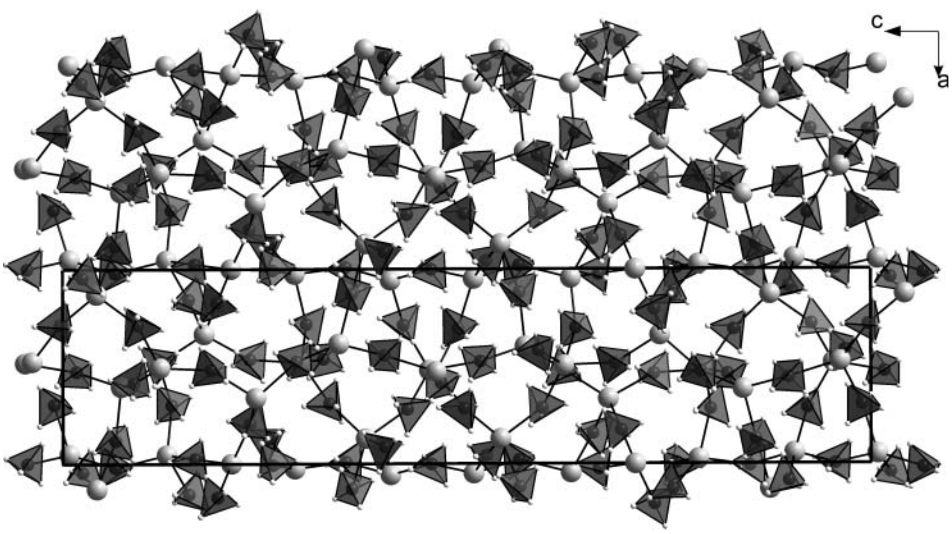


Fig. 1. Structure of $Mg(BH_4)_2$ viewed along the hexagonal *b* axis, showing two unit cells [Černý *et al.* (2007)]. Dark grey (partially transparent) tetrahedra are BH_4 units; Mg atoms in light grey.

Table 1. Metal and chemical hydrides characterized by using the program Fox [Favre-Nicolin and Černý (2002)], and ordered according to the structural complexity. The space group, cell volume, number of symmetry independent atoms solved *ab initio*, diffraction data used (X – laboratory powder X-rays, X (*s.c.*) – laboratory single crystal X-rays, S – powder synchrotron, N – powder neutron) and reference are given.

Formula	Symmetry	Cell volume [Å^3]	Non-H + H atoms	Data	Ref.
α-$Li_2Mg(NH)_2$	$Iba2$	254	3 + 1	S + N	Rijssenbeek *et al.* (2007)
$LiBH_4$-RT	$Pnma$	217	2 + 3	S	Soulié *et al.* (2002)
$LiBH_4$-HT	$P6_3mc$	110	2 + 2	S	Soulié *et al.* (2002)
$LiBH_4$-HP	$Ama2$	181	2 + 3	S	Filinchuk *et al.* (2008)
$NaBH_4$-HP	$Pnma$	167	2 + 3	S	Filinchuk *et al.* (2007a)
Li_3AlD_6	$R\bar{3}$	537	3 + 2	S + N	Brinks and Hauback (2003)
Li_4Tt_2D, Tt = Si, Ge	$Cmmm$	187, 195	4 + 1	N	Wu *et al.* (2007)
γ-AlD_3	$Pnnm$	227	2 + 4	S + N S	Brinks *et al.* (2007) Yartys *et al.* (2007)
$Ce_2Ni_7D_{\sim 4}$	$Pmcn$	1232	0 + 8	N	Filinchuk *et al.* (2007b)
$Zr_2CuH_{\sim 5}$	$I2/m$	272	3 + 5	S + N	Filinchuk and Yvon (2005b)
$NdNi_4MgD_{3.6}$	$Pmn2_1$	205	5 + 3	S + N	Guénée *et al.* (2003)
$CsMgD_3$	$Pmmn$	522	4 + 5	S + N	Renaudin *et al.* (2003a)
$Zr_3NiO_{0.6}D_{6.58}$	$Cmcm$	382	4 + 5	S + N	Zavaliy, I. Yu. *et al.* (2003)
$LaMg_2PdD_7$	$P2_12_12_1$	453	4 + 7	S + N	Yvon *et al.* (2007)
$Li_4BN_3H_{10}$	$I2_13$	1218	5 + 0	X(*s.c.*)	Filinchuk *et al.* (2006)
$LaNi_2Mn_3D_{5.6}$	$P6/mmm$	361	5 + 5	S + N	Guénée and Yvon (2003)
$Zr_9V_4SD_{23}$	$P6_3/mmc$	684	5 + 5	S + N	Zavaliy, I. Yu. *et al.* (2005)
$ErFe_2D_5$	$Pmn2_1$	249	5 + 8	N	Paul-Boncour *et al.* (2003)
$LiMg(AlD_4)_3$	$P2_1/c$	859	5 + 12	S + N	Grove *et al.* (2007)
$Li_{2+x}MgN_2D_{2-x}$ – interm. phase	$P\bar{4}3m$	127	6 + 1	S + N	Nakamura *et al.* (2007)
Li_2BeD_4	$P2_1/c$	491	6 + 8	X + N	Bulychev *et al.* (2004)
$LaMg_2NiD_7$	$P2_1/c$	860	8 + 14	S + N	Renaudin *et al.* (2003b)
$La_2MgNi_2H_8$	$P2_1/c$	1107	10 + 16	S + N	Chotard *et al.* (2006)
$Mg(BD_4)_2{}^a$	$P6_1$	3411	15 + 40	S + N	Černý *et al.* (2007)

a: It has been shown recently that the true symmetry is $P6_122$ (Filinchuk, Černý and Hagemann, provate communication).

for indexing. In the DSM approach, the structure was modeled 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 [Favre-Nicolin and Černý (2002)]. The correct structure was recognized after several hours of optimization. In the RSM approach, the structure was solved with the aid of the program EXPO [Altomare *et al.* (2004)] 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 (see below) keeping the borohydride groups rigid.

The most popular DSM program in the non-molecular world is Fox [Favre-Nicolin and Černý (2002)]. Since its release in 2001 the program has been frequently used for solving crystal structures of hydrides from powder diffraction data [Černý and Favre-Nicolin (2005)]. The complexity of the structures solved ranges from 2 to 55 independent atoms (see Table 1). Guidelines for efficient use of Fox can be found in [Černý and Favre-Nicolin (2007)].

Completing the structural model

The initial structural model obtained from DSM or RSM does not always reveal all the atoms or details of the structure. The model must be completed either by analysis of difference Fourier maps [Giacovazzo (2002)] or by a crystal chemistry analysis. The structure of $LaMg_2NiH_7$ [Renaudin *et al.* (2003b)] is an example where the final metal-hydrogen complexes, the correct building blocks, NiH_4 were recognized *a posteriori* after having solved the structure by DSM and modeling with free atoms. The metal atom substructure was modeled with two La, two Ni and four Mg free atoms that were easily located from synchrotron data. Fourteen D sites in general position 4*e* of the space group $P2_1/c$ were located from neutron data keeping the metal atoms positions fixed. From subsequent optimization of the D sites occupation, it was found that the structure was fully ordered, and two independent NiD_4 complexes and six ionic D atoms in the unit cell were recognized.

In the case of $La_2MgNi_2H_8$ [Chotard *et al.* (2006)], the situation was even more peculiar. Two sorts of polynuclear complexes, Ni_2H_7 and Ni_4H_{12}, were recognized in the structural model after optimization using the Fox program. The starting configuration was modeled with free La and Mg atoms and tetrahedral building blocks NiD_4. The tetrahedra were moved to the positions where they shared one or two D ligands which resulted in the polynuclear complexes.

Refinement by Rietveld method

The refinement of the final structural model against powder patterns is nowadays done exclusively by the Rietveld method. For details of the method see for example [Young (1993)] and for guidelines see [McCusker *et al.* (1999)]. Three programs are used mostly, depending on the user's preference, when refining hydride structures: FullProf [Rodríguez-Carvajal (1993)], TOPAS [Coelho (2004)] and GSAS [Larson and Von Dreele (2004)]. All three programs allow for joint refinement of several powder patterns, typically X-ray and neutron data, rigid body modelling (as it was the case of TOPAS and $Mg(BH_4)_2$), anisotropic line broadening modelling (see below), treatment of time-of-flight (ToF) neutron data. FullProf and TOPAS allow so-called sequential refinement, *i.e.* refinement of many powder patterns as function of temperature, pressure etc. [Joubert *et al.* (2006)].

It is well known that the precision of structural parameters is overestimated in the Rietveld refinement resulting from serial correlations in the observed data and non-accessibility of the goodness-of-fit parameter based on integrated intensities of individual reflections. Several theoretical models were proposed to correct this handicap, see Chapter 10 in [McCusker *et al.* (1999)], and [David (2004)] has provided the correct statistical analysis to address this issue. The multiplication factor for standard uncertainties of structural parameters obtained from Rietveld refinement according to these analyses is typically in the range 3–5.

Localization of hydrogen from X-ray data only

In the case of lightweight hydrides, hydrogen becomes a non-negligible scatterer. $LiBH_4$ is an example of a hydride structure for which the hydrogen atoms have been located unambiguously only by XPD [Soulié *et al.* (2002)]. Although the precision of the metal-hydrogen bond lengths obtained is lower than that usually attained by neutron diffraction, they were useful for a crystal chemical discussion. The orthorhombic structure was modeled within DSM by one BH_4 group and one Li atom as deduced from the chemical formula, cell volume and the multiplicity of the general Wyckoff site. The model converged within a few cycles to the correct structure. The BH_4 tetrahedra were kept as semi-rigid units.

Since then synchrotron radiation alone has been used more often for studying light metal borohydrides such as the high pressure phases of $LiBH_4$ [Filinchuk *et al.* (2008)]. The typical setup for these measurements is an area detector in Debye-Scherrer geometry. The advantage of this setup is the simple sample environment and fast data collection which allows *in-situ* studies, high data collection rates that provide highly accurate measured intensities, and a lower sensitivity to preferred orientation effects.

Apparently powder samples

It is possible to find a single grain of sufficient size for XSD in a apparently powder hydride sample, as was the case for $Li_4BN_3H_{10}$ [Filinchuk *et al.* (2006)]. Samples were prepared from 2 : 1 mixtures of $LiNH_2$ and $LiBH_4$, and the reaction products were enclosed in sealed capillary tubes, remelted, and examined on a powder X-ray diffractometer. The best specimens were selected and the capillary was examined on a single crystal diffractometer equipped with an image-plate detector and a MoK_α radiation. The segment giving the best individual diffracting spots and practically no Debye rings was selected for measurement. A satisfactory model was obtained by DSM (program Fox) in space group $I2_13$, yielding one N, one B, and three symmetry-independent Li sites. Subsequent difference Fourier maps revealed four H positions, and the structure refined by a standard least-square procedure. Independently, the structure was characterized from XPD (synchrotron) and NPD (ToF) [Chater *et al.* (2006)]. The B and N atoms were localized from XPD (DSM program TOPAS). Positions of Li atoms were determined from the structural similarity to $LiNH_2$ and verified by Rietveld refinement with synchrotron data. The same strategy, involving neutron data collected on natural sample without isotopic enrichment, was used to localize the H atoms. Two independent structural determinations provided results which are identical within the accuracy of both experiments. Typically, the single crystal work is one order of magnitude superior in the precision of atomic coordinates; on the other hand the powder work is more than one order of magnitude superior in the precision of lattice parameters.

Structure databases and structure prediction

To our best knowledge, the only database specialized on hydrides and providing the information on crystal structure is the hydride fluoride crystal structure database, HFD [Gingl, Gelato and Yvon (1997)]. The primary motivation for creating HFD was to predict new metal hydrides from the structural analogies with metal fluorides. The database contains complete structural information on published hydrides and fluorides. The crystal structure information of hydrides can be found in several crystallographic databases of inorganic compounds; in particular, the Inorganic Crystal Structure Database [Bergerhoff and Brown (1987)], Pearson's Crystal Data [Villars and Cenzual (2007/8)] and Crystallography Open Database (http://www.crystallography.net/).

Significant effort is currently underway in the structure prediction of hydrides. Predictions are often based on the analysis of multi-element systems with the idea of determining potentially interesting compounds for hydrogen storage. Structural predictions of metal hydrides began with simple geometrical analysis. The interstitial sites in the metal matrix of intermetallic compounds which can be potentially occupied by hydrogen can be predicted based only on geometrical criteria: a minimum radius of 0.40 Å of a sphere which can be accommodated on the site [Westlake (1983)], and a minimum H–H distance of 2.1 Å [Switendick (1979)]. The particular predicted sites that are filled by hydrogen can be determined by refinement of occupancy factors using neutron data. Nowadays the simple geometric criteria are easily interpreted in DSM as anti-bump distance penalty function, for example in the program Fox [Favre-Nicolin and Černý (2002)].

The *ab-initio* prediction of the crystal structure of hydrides from first principles is still not routine. A typical method applied is Density Functional Theory (DFT) based optimization of several structural models proposed from the composition, atomic size, and electronic state similarities with known compounds. The structural model with minimal total energy is taken to be the predicted structure. The method can find the correct structure usually in the case of simpler atomic arrangements such as $KAlH_4$ [Vajeeston *et al.* (2004)], but fails with more complex structures such as $Mg(BH_4)_2$ where three different structural models were predicted [Nakamori *et al.* (2006), Vajeeston *et al.* (2006)], but they succeeded only partly to predict the correct magnesium coordination [Černý *et al.* (2007)] and failed on the longer range structure. Neglected structural disorder or nonharmonic vibrations can even make the DFT optimization converge to a false minimum as is the case of high temperature form of $LiBH_4$ which was experimentally observed as hexagonal [Soulié *et al.* (2002), Hartman *et al.* (2007)] but predicted as monoclinic [Łodziana and Vegge (2004)].

Problems and solutions

Impurity phases

Solid state route synthesis from powders at high pressures (up to 160 bar) of hydrogen atmosphere and moderate temperatures (<700 °C) is a method often used for the preparation of metal hydrides. The resulting products sometimes contain more than one phase. Unreacted starting components, oxides and other hydrides can be present. Modern methods of powder pattern decomposition and indexing are needed and high resolution powder diffraction data are necessary in the case of multiphase samples. The correct indexing of the powder pattern of a new unknown hydride is only possible after successful qualitative phase analysis of the sample. Rietveld refinement usually converges successfully for the correct structural model even in the case of a multiphase sample. Due to a different diffraction contrast of X-ray and neutron data some of the impurities are detectable only in neutron patterns (LiD, MgO).

Occupation disorder on hydrogen sites, merging excess hydrogen atoms

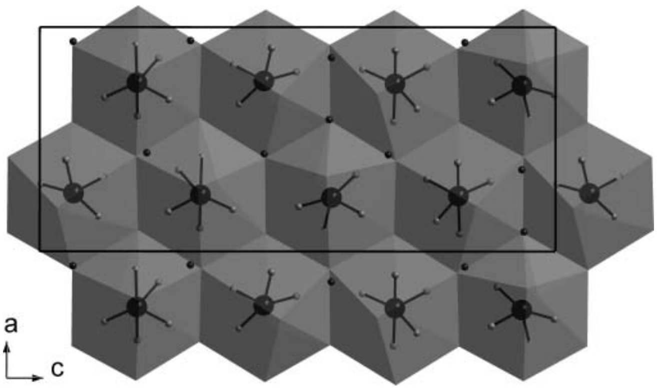
To describe a crystal structure adequately for global optimization when DSM is applied, it is necessary to take into account the connectivity between the individual building blocks such as the coordination polyhedra. This is achieved in the program Fox by applying a dynamic occupancy correction (DOC) which also handles the high symmetry atomic sites (Wyckoff sites) in the unit cell [Favre-Nicolin and Černý (2002)]. It was later recognized that DOC is an ideal tool to treat the uncertainty of hydrogen content and sites occupation by hydrogen in interstitial hydrides. When H atoms are dissolved in the crystal lattice of an intermetallic compound, usually a great number of interstitial sites, typically the tetrahedral holes, can be occupied by hydrogen. These sites are, however, too close one to another to be simultaneously occupied by H atoms according to the Switendick rule [Switendick (1979)]. It leads to partially occupied hydrogen sites and an uncertainty in the number of Wyckoff sites occupied by hydrogen. The DOC can easily treat this problem. The starting model for the global optimization in DSM can contain more H atoms than needed for the correct structure. The excess hydrogen atoms are simply merged by DOC. It means that when optimizing the structural model with Fox one does not need to specify at the beginning which Wyckoff sites (special or general) will be occupied by individual atoms, what is the connectivity between the building blocks (like sharing vertices between polyhedra) and even what is the exact chemical composition of the crystal. The only condition is that the starting model contains at least the correct number (or more) of independent structural building blocks.

Weak superstructures and strong pseudo-symmetry of metal lattice

The arrangement of metal atoms in metal hydrides usually shows a small deviation from an arrangement with higher symmetry or shorter periodicity. This deviation is created by positioning H atoms in the matrix of metal atoms (it does not necessarily exist without hydrogen) which becomes then only slightly deformed. Because of the 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; both are clearly visible only in neutron patterns. X-ray patterns with low background are needed to detect the weak superstructure peaks. High angular resolution is necessary in both X-ray and neutron patterns to separate overlapping peaks and to detect the correct symmetry of the structure. The true symmetry can generally be revealed with confidence after successful indexing of the neutron powder pattern.

An example of a weak superstructure is $Mg_6Co_2H_{11}$ [Černý *et al.* (1992)]. Its crystal structure (*Pnma*, $a = 8.1120(1)$, $b = 10.0800(1)$, $c = 18.6028(3)$ Å) was solved and refined jointly from one synchrotron (NSLS Brookhaven, $\lambda = 1.6295$ Å) and two neutron powder patterns (ILL Grenoble, $\lambda = 1.5939$ Å and PSI Villigen, $\lambda = 1.7070$ Å). The angular resolution of both neutron experiments was optimized at different 2θ regions, the ILL data were better at high angles and PSI data at low angles. The metal atoms were localized from synchrotron Patterson and Fourier maps of a four times smaller subcell along the *c*-axis, which is the average periodicity of the metal lattice (Fig. 2(left). Only a careful analysis of very weak superstructure peaks in the synchrotron pattern has revealed the true periodicity and allowed the refinement of the occupation of 20 proposed D sites (based on minimal interatomic distances) from both neutron patterns. The true periodicity is clearly seen only in the neutron data. See Fig. 2(right), where the strongest neutron superstructure reflections are marked as 1 and 2. They are nearly invisible in the synchrotron data where the triplet of strongest superstructure reflections is marked too.

An example of strong pseudo-symmetry of the metal lattice is $LaMg_2NiH_7$ [Renaudin *et al.* (2003b)]. X-ray la-



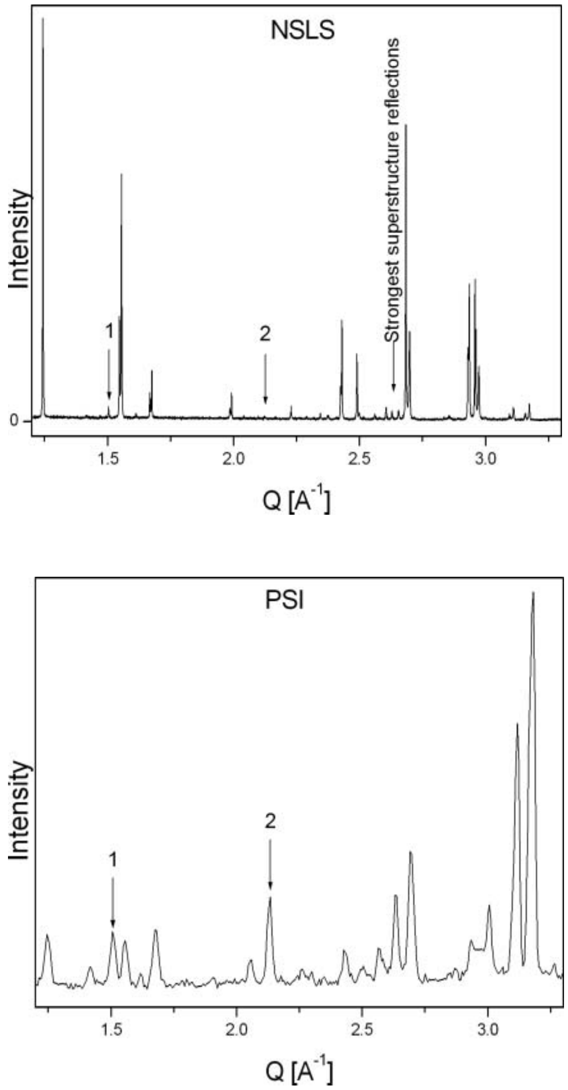


Fig. 2. (Left) One (101) layer of $Mg_6Co_2H_{11}$ structure (*Pnma*) viewed along the orthorhombic *a*-axis [Černý *et al.* (1992)]. Dark grey (partially transparent) polyhedra are Mg_8 cubes centered with CoH_4 and CoH_5 complexes. Cobalt atoms as bigger and hydrogen atoms as smaller spheres, the anionic hydrogen in dark.

(Right) The four times shorter periodicity of the average structure of metal lattice is visible in low intensity of superstructure reflections in synchrotron pattern (NSLS) compared to the average structure (*Cmcm*) reflections. The true periodicity is clearly seen only in the neutron pattern (PSI), where the strongest neutron superstructure reflections are marked as 1 and 2. They are nearly invisible in the synchrotron data where the triplet of strongest superstructure reflections is marked too.

boratory data can be explained with the orthorhombic symmetry *Pnma*, and only high resolution synchrotron data has allowed identify the true monoclinic symmetry $P2_1/c$ which was then confirmed by NPD. Another example is $SrMgD_4$ [Gingl, Yvon and Fischer (1992)] whose X-ray data refines very well in the space group *Cmcm* while the true symmetry is $Cmc2_1$.

Anisotropic line broadening

Broadening of diffraction lines decreases the resolving power of a powder pattern and complicates the structure solution procedure as the intensities of individual reflections cannot be determined unambiguously. When the broadening becomes anisotropic (*hkl*-dependent, i.e. it depends on the direction in the reciprocal space) its modeling in Rietveld refinement becomes complex.

Example of strain-size induced anisotropic line broadening is $LaNi_5H_6$ hydride [Lartigue, Le Bail and Percheron-Guégan (1987)]. The anisotropic micro-strain is induced by the misfit dislocations between α and β phases created during the first cycle of hydrogen absorption. The broadening can be qualitatively modeled by empirical models, such as the general model proposed by [Stephens (1999)]. Quantitative modeling allowing also the determination of dislocation type and density [Wu *et al.* (1998), Černý *et al.* (2000)] was possible by applying the theory of Krivoglaz [Krivoglaz (1969)] modified for hexagonal symmetry in [Klimanek and Kužel (1988, 1989)].

Examples of micro-twinning induced anisotropic line broadening include Mg_2NiH_4 [Zolliker, Yvon and Baerlocher (1986)] and $Mg_6Ir_2H_{11}$ [Černý *et al.* (2002)]. Mg_2NiH_4 undergoes a structural phase transition from a disordered, cubic high temperature modification into an ordered, monoclinic low temperature modification. As two orientations of the monoclinic lattice related to the parent cubic lattice are possible, the resulting crystals of the LT-modification contain domains with both orientations related by a twin operation of a mirror repeated with a given probability on the microscopic scale – micro-twinning. The resultant anisotropic line broadening has hindered for a long time the structural characterization of the LT-phase, which only became possible when the broadening was understood and modeled on the basis of the theory of Cowley and Au (1978). The micro-twinning in monoclinic $Mg_6Ir_2H_{11}$, which is a deformation variant of orthorhombic $Mg_6Co_2H_{11}$, is due to the orthorhombic pseudo-symmetry of a monoclinic lattice (monoclinic angle $\beta = 91.03(1)°$). The broadening was successfully modeled [Černý, Joubert and Yvon (1998)] by a general recursion algorithm for calculating kinematical diffraction intensities from crystals containing coherent planar faults [Treacy, Newsam and Deem (1991)].

Bad powder data

The synthesis of metal hydrides by absorption of hydrogen in the metal lattice can sometimes render impossible preparation of powder samples with good crystallinity as was the case of $Zr_2CuH_{\sim 5}$ [Filinchuk and Yvon (2005b)]. A complete reconstruction of the metal lattice after hydrogen absorption resulted in powder patterns of low quality. The indexing of X-ray data proved to be intractable with laboratory source, and was achieved only with synchrotron data ($I2/m$, $a = 9.3514(12)$, $b = 3.5784(6)$, $c = 8.3628(18)$ Å, $\beta = 104.301(13)°$). Two Zr positions and one Cu position were located from the synchrotron data, while five D sites were located by using the neutron data; both stages used the program Fox. The line broadening is due to strain and not size effects, and it was modeled during the Rietveld refinement using the program Fullprof. Rather than limits of DSM with respect to the quality of diffraction data this example shows again that the bottleneck of SDPD can often be indexing.

Strongly textured sample

In extreme conditions of a high pressure cell, the *ab initio* structural characterization of new high pressure phases is often complicated by a strong preferred orientation of grains in a powder sample – texture. When working with DSM, texture can be optimized jointly with the structural model. The first example of successful structure solution on strongly textured sample is the high pressure phase of $NaBH_4$ ($BaSO_4$-type structure, $Pnma$, $a = 7.2970(11)$, $b = 4.1166(5)$, $c = 5.5692(7)$ Å at 11.2 GPa) [Filinchuk *et al.* (2007a)]. The preferentially oriented plane (h00) was identified and the magnitude of the texture optimized jointly with the positions of one Na atom and one BH_4 group. The presence of texture in a standard PD experiments depends mostly on the shape anisotropy of grains in the powder sample, and it can be minimized (as discussed above) by using Debye-Scherrer geometry in combination with an area detector.

Chemical and positional disorder

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 if the scattering contrast between the metals is strong enough. Two options are available: the joint refinement of X-ray and neutron data or the use of resonant scattering. Note that for the case of n atomic species (including vacancies) on one site, one needs n_1 diffraction patterns with different contrast between the scatterers in question. An example of the analysis of multi-substituted $LaNi_5$ alloy is given in [Joubert *et al.* (1998)].

As discussed earlier, the simple geometrical rule of a minimal H–H separation [Switendick (1979)] excludes simultaneous occupation of two interstitial sites closer than this minimal distance (2.1 Å). This leads to partial occupied (disordered) H sites. The average metal matrix symmetry is often conserved in room- or high-temperature phases as observed from Bragg intensities which are used in Rietveld refinement. At lower temperatures, the H atoms very often order on interstitial sites, the symmetry is lowered and a fully ordered coordination of metals by H atoms can be obtained. Whether the H atoms are locally ordered already in the disordered phase can be studied from the diffuse intensity of the scattered radiation. The diffuse scattering from polycrystalline samples can be studied by using the PDF analysis; for more details about the method see [Egami and Billinge (2003)]. The PDF technique was applied in the analysis of local hydrogen ordering in the cubic Laves phases $ZrCr_2D_4$ [Sørby *et al.* (2008)], YMn_2D_x and YFe_2D_x [Ropka, Černý and Paul-Boncour (2008)].

Conclusions

Structural characterization of hydrides is currently undertaken mostly by X-ray and neutron diffraction with deuterated samples for neutron diffraction. In the case of lightweight hydrides like borohydrides of light alkaline metals/earths, X-ray diffraction alone can provide structural parameters with sufficient accuracy. A crystallographer analyzing hydrides has to face numerous crystallographic challenges which include: complex structures, superstructures, pseudo-symmetries, twinning, chemical and positional disorder, structural solution from low quality data (powder patterns), joint use of several data sets, resonant scattering and fast *in-situ* data collection.

Structural characterization with single crystals, even if more precise than with powders, is unusual, because of the lack of single crystals due to the solid state synthesis. However, a small number of significant studies such as *in-situ* hydrogenation of a single crystal or single grain analysis of an apparently powder sample have been performed.

Powder diffraction dominates the structural analysis of hydrides. The structural results obtained since the beginning of the use of powder diffraction, and especially within the last 15 years, show the power of this method. Crystal structures containing as many as 55 independent atoms (including hydrogen) have been fully characterized by the powder diffraction. This is of great importance, because rapid collection of powder data thanks to modern synchrotron and neutron sources opens up the possibility for fast *in-situ* studies, mapping of phase transitions induced by the temperature, pressure, hydrogen content, and chemical reactions. The progress in structural characterization of hydrides goes hand in hand with the progress in the powder diffraction methodology. The Direct Space Methods are currently the powder diffraction methods mostly used in hydride research for their simplicity of use, ability to work with powder patterns of low quality (broad peaks), easy way to treat the occupation disorder on hydrogen sites and active use of simple geometrical constraints.

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