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Light metal borohydrides: crystal structures and beyond

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Abstract. Experimental structures of $M(BH_4)_n$, where M is a 2nd–4th period element, are reviewed with a particluar emphasize on crystal chemistry. It is shown that except certain cases, the BH_4 group has a nearly ideal tetrahedral geometry. Correction of the experimentally determined H-positions allows to compare directly the results obtained by different diffraction techniques and by theoretical calculations. Analysis of coordination geometries for M and BH_4, and of mechanisms of phase transitions in $LiBH_4$, suggests that the directional $BH_4 \ldots M$ interaction is at the origin of structural complexity of borohydrides. The ways to influence their stability by chemical modification are discussed. Study of structural evolution with temperature and pressure is shown to be the way to access fundamental information on structural stability of these systems.

Introduction

Borohydrides, also called tetrahydridoborates, are largely ionic compounds with a general formula $M(BH_4)_n$, consisting of metal cations M^{n+} and borohydride anions BH_4^-. Due to a high weight percent of hydrogen, they are considered as prospective hydrogen storage materials. Indeed, some borohydrides desorb a large quantity of hydrogen (up to 20.8%), although the decompositon temperatures are usually high. Different fundamental aspects of the use of light metal hydrides, including borohydrides, for the storage and production of hydrogen have been comprehensively reviewed by Grochala and Edwards, 2004. Thermodymanic properties of metal borohydrides with respect to their hydrogen storage applications were recently briefly reviewed by Soloveichik, 2007. These and other (Orimo *et al.*, 2007; Züttel *et al.*, 2007) reviews covering borohydrides have no special focus on their crystal structure. Our short review is aiming to close this gap.

Almost all borohydrides are crystalline solids already at room temperature. This gives an advantage of using diffraction methods to study their structure. Diffraction provides an immense ammount of information not only about the structure, but also is more and more frequently used now for screening and characterization of new substances, reaction products and intermediates. Detailed diffraction study of a promising material at various temperatures and pressures allows to uncover new polymorphs, follow their structural evolution and therefore get a clue to understand (and maybe even alter) the thermodymanic stability. This review will be mostly focused on crystal structures of known metal borohydride phases, also aiming to give a feeling about how much modern diffraction techniques can go beyond a simple structure characterization.

We will review here the experimentally observed structures of light borohydrides $M(BH_4)_n$, where by "light" we assume M to be an element of the 2nd to the early 4th period. Since the most of the theoretically predicted structures remain hypothetical, this review is limited to the experimentally observed ones. The known metal borohydride phases and their crystallographic characteristics are summarized in Table 1. The Table, and this short review do not pretend to be exhaustive, so only one (normally the first) work aiming to determine the crystal structure using a given diffraction technique is mentioned here.

Crystal structures

$LiBH_4$

Four $LiBH_4$ phases are known: two at ambient and two at high pressure. The first structural study of the ambient pressure polymorphs was made using synchrotron powder diffraction by Soulié *et al.*, 2002. The low-temperature structure has *Pnma* symmetry. It transforms into a hexagonal wurtzite-like high-temperature phase at ~380 K.

Since the originally proposed $P6_3mc$ symmetry of the high-temperature phase has been questioned by theoreticians, it has been revisited by neutron powder diffraction on the triply isotopically substituted $^7Li^{11}BD_4$ (Hartman *et al.*, 2007) and by synchrotron diffraction on single crystals and powder (Filinchuk, Chernyshov, 2007; Filinchuk *et al.*, 2008a). These recent studies confirm the $P6_3mc$ space group symmetry for the high-temperature phase, and reveal large and anisotropic displacements for hydrogen atoms. The observed atomic displacement ellipsoids (Fig. 1b) may indicate, in addition to the thermal vibrations, an orientational disorder (hindered rotations) of the BH_4 group. Large libration amplitudes in the hexagonal

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Table 1. Known phases of light metal borohydrides and their crystallographic characteristics.

Compound	Space group	a (Å)	b (Å) β (°)	c (Å)	Method[a]	Experimental conditions[b]	Ref.
$LiBH_4$	*Pnma*	7.17858(4)	4.43686(2)	6.80321(4)	XRPD	293 K	Soulié *et al.*, 2002
		7.1213(2)	4.4060(1)	6.6744(2)	NPD	3.5 K	Hartman *et al.*, 2007
		7.141(5)	4.431(3)	6.748(4)	SCXRD	225 K	Filinchuk *et al.*, 2008a
	$P6_3mc$	4.27631(5)		6.94844(8)	XRPD	408 K	Soulié *et al.*, 2002
		4.2667(2)		6.9223(8)	NPD	400 K	Hartman *et al.*, 2007
		4.3228(10)		7.0368(10)	SCXRD	535 K	Filinchuk *et al.*, 2008a
	*Ama*2	6.4494(9)	5.307(1)	5.2919(9)	XRPD	293 K, 2.4 GPa	Filinchuk *et al.*, 2008b
	$Fm\bar{3}m$	5.109(2)			XRPD	293 K, 18.1 GPa	Filinchuk *et al.*, 2008b
$NaBH_4$	$Fm\bar{3}m$	6.148(1)			NPD	293 K	Fischer, Züttel, 2004
		6.1308(1)			SCXRD	200 K	Filinchuk, Hagemann, 2008
	$P\bar{4}2_1c$	4.332(1)		5.869(1)	NPD	10 K	Fischer, Züttel, 2004
	Pnma	7.297(1)	4.1166(5)	5.5692(7)	XRPD	293 K, 11.2 GPa	Filinchuk *et al.*, 2007
KBH_4	$Fm\bar{3}m$	6.728(1)			SCXRD	293 K	Luck, Schelter, 1999
		6.7306(1)			NPD	295 K	Renaudin *et al.*, 2004
	$P4_2/nmc$	4.7004(2)		6.5979(3)	NPD	1.5 K	Renaudin *et al.*, 2004
$Be(BH_4)_2$	$I4_1cd$	13.62(1)		9.10(1)	SCXRD	293 K	Marynick, Lipscomb, 1972
$Mg(BH_4)_2$	$P6_1$	10.3182(1)		36.9983(5)	XRPD + NPD	293 K	Černý *et al.*, 2007
	Fddd	37.072(1)	18.6476(6)	10.9123(3)	XRPD	293 K	Her *et al.*, 2007
$Ca(BH_4)_2$	*Fddd*	8.791(1)	13.137(1)	7.500(1)	XRPD	293 K	Miwa *et al.*, 2006
	*F*2*dd*	8.7759(3)	13.0234(4)	7.4132(2)	XRPD	91 K	Filinchuk *et al.*, 2008c
	$P4_2/m$	6.9468(1)		4.3661(1)	XRPD + NPD	480 K	Buchter *et al.*, 2008
	$P\bar{4}$	6.9189(1)		4.3471(1)	XRPD	305 K	Filinchuk *et al.*, 2008c
	$I\bar{4}2d$	5.8446(3)		13.228(1)	XRPD	495 K	Filinchuk *et al.*, 2008c
$Al(BH_4)_3$	*C*2/*c*	21.917(4)	5.986(1)	111.90(3) 21.787(4)	SCXRD	150 K	Aldridge *et al.*, 1997
	$Pna2_1$	18.021(3)	6.138(2)	6.199(1)	SCXRD	195 K	Aldridge *et al.*, 1997
$LiK(BH_4)_2$	*Pnma*	7.91337(5)	4.49067(3)	13.8440(1)	XRPD	293 K	Nickels *et al.*, 2008
$LiSc(BH_4)_4$	$P\bar{4}2c$	6.07593(6)		12.0338(1)	XRPD	293 K	Hagemann *et al.*, 2008

a: SCXRD – single-crystal X-ray or synchrotron diffraction, XRPD – X-ray or synchrotron powder diffraction, NPD – neutron powder diffraction.
b: Ambient pressure is assumed if not otherwise specified.

phase agree with an apparent shortening of the B–H bonds to ~1.07 Å. An entropy contribution from the disorder is considered as a factor stabilizing the hexagonal structure (Filinchuk, Chernyshov, 2007; Filinchuk *et al.*, 2008a).

Single crystal investigation of the *Pnma* phase at 225 K unambiguously shows that the BH_4 group has a nearly ideal tetrahedral geometry, in contrast to strongly distorted tetrahedra reported in earlier synchrotron diffraction studies (Soulié *et al.*, 2002; Züttel *et al.*, 2003). The observed H–B–H angles, 108.8(9)–109.9(7)°, are very close to the ideal tetrahedral angle of 109.5°, and the B–H bond lengths show a narrow spread from 1.104(11) to 1.131(15) Å. Neutron diffraction at 3.5 K also shows that the BH_4 group is very close to the undistorted tetrahedron: B–H distances are 1.208(3)–1.225(6) Å, H–B–H angles – 107.2(3)–111.7(4)°.

The two ambient pressure phases have similar structures (Figs. 1a and 1b), where Li atoms and BH_4 groups are tetrahedrally coordinated. In the orthorhombic phase at 225 K, Li–B distances are 2.37–2.57 Å. In the hexagonal phase at 535 K, there are three short B–Li contacts of 2.55 Å in the basal plane and one long of 3.00 Å along the *c* axis.

At room temperature and a pressure of 1.2–10 GPa, $LiBH_4$ forms a new phase with pseudo-tetragonal *Ama*2 structure (Filinchuk *et al.*, 2008b). It can be considered as an orthorhombically distorted antistructure of PtS, where Li atoms are tetrahedrally coordinated by BH_4 groups (Li–B distances of 2.35–2.66 Å) and the BH_4 group has a totally new nearly square-planar coordination by four Li atoms (Fig. 1c). Above 10 GPa another $LiBH_4$ phase forms (Filinchuk *et al.*, 2008b). It is isostructural to the cubic $NaBH_4$ (see below); Li atoms and BH_4 groups are octahedrally coordinated (at 18 GPa, the Li–B distances are 2.56 Å). In the *Ama*2 phase, the geometry of the BH_4^- anions was restrained to an ideal tetrahedron with the B–H bond lengths centered at ~1.17 Å, while in the cubic phase at 18.1 GPa the refined B-H distance is 1.08 Å.

The borohydride groups are connected to Li atoms mostly via the tetrahedral edges. However, in the hexagonal phase and in the case of the shortest Li–B contact (2.37 Å) in the *Pnma* phase, the borohydride groups are connected to Li atoms via the tetrahedral faces.

$NaBH_4$

Under ambient conditions $NaBH_4$ has a cubic structure, isomorphous to NaCl. From the diffraction data alone, this structure can be desribed in either $Fm\bar{3}m$ or $F\bar{4}3m$ space groups. The two models differ only by the absence of the

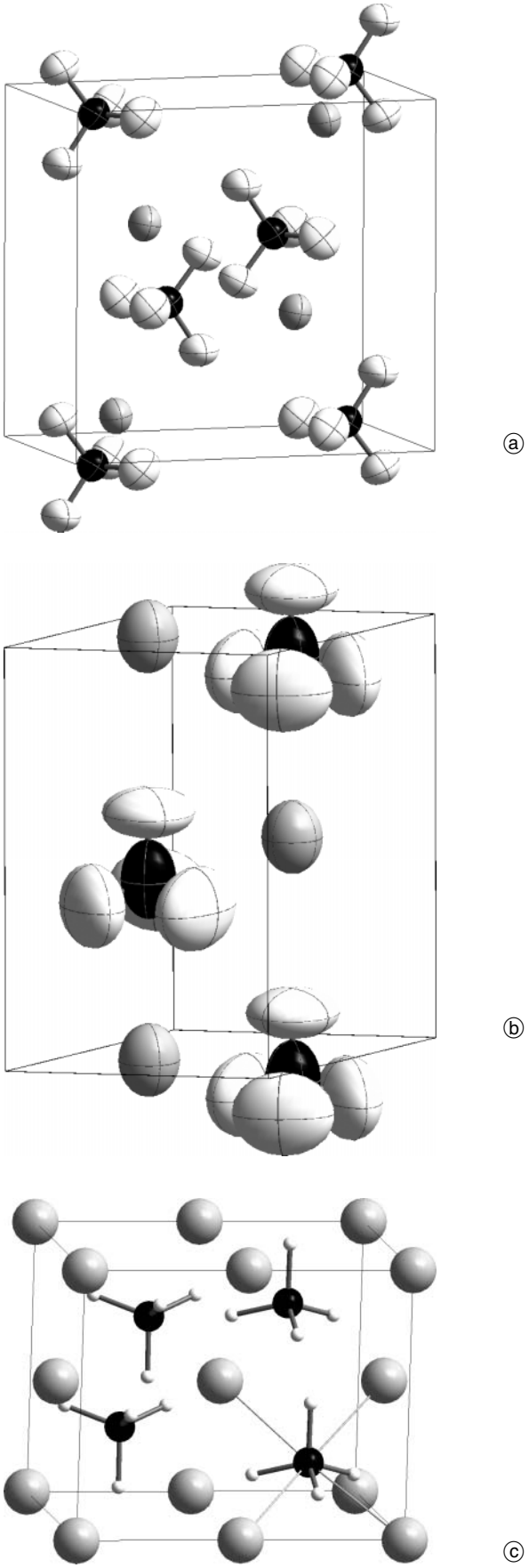

Fig. 1. Crystal structure of the $LiBH_4$ phases: *Pnma* (**a**), $P6_3mc$ (**b**) and *Ama*2 (**c**). The cubic $Fm\bar{3}m$ structure is identical to the one presented in Fig. 2a. Anisotropic displacement ellipsoids determined from synchrotron diffraction on single crystals (Filinchuk *et al.*, 2008a) are shown for the ambient pressure phases.

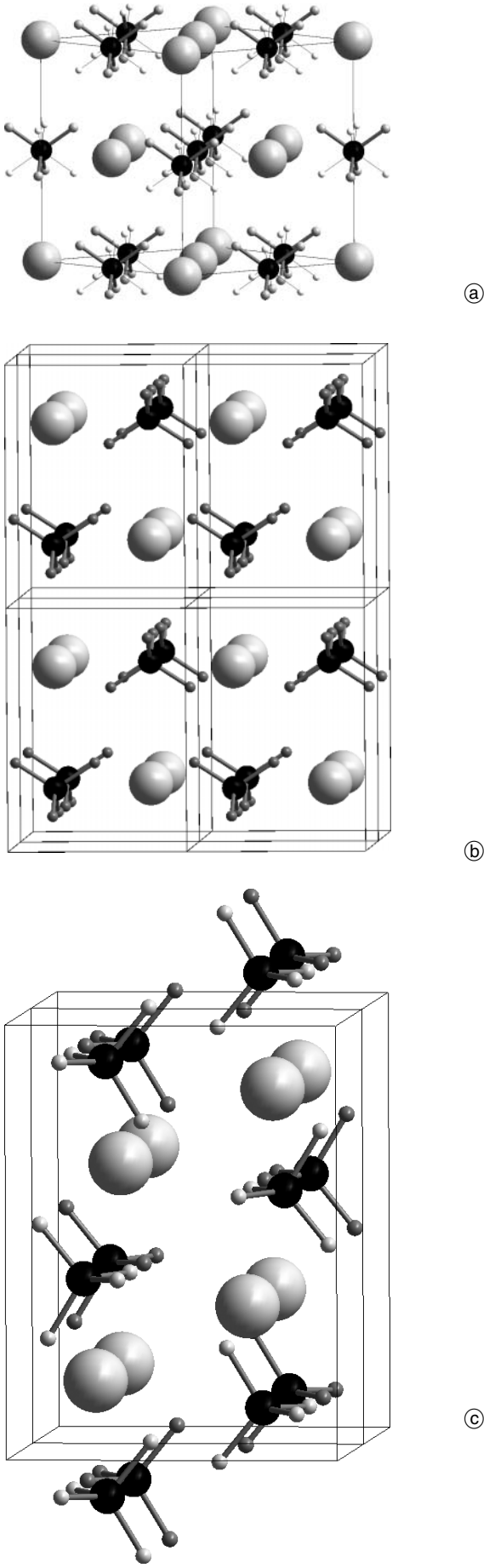

Fig. 2. Crystal structure of the $NaBH_4$ phases: $Fm\bar{3}m$ (**a**), $P\bar{4}2_1c$ or $P4_2/nmc$ (**b**) and *Pnma* (**c**).

inversion centre in $F\bar{4}3m$. The centrosymmetric model is intrinsically disordered, showing two orientations of the BH_4^- group (Fig. 2a), while the non-centrosymmetric model allows the BH_4^- anion to be fully or partly ordered. A peak of heat capacity at ~190 K (Johnston, Hallett, 1953) suggests an order-disorder transition. The estimated entalpy of the transition is consistent with a transformation from the fully orientationally disordered high-tempreture cubic phase to an ordered low-temperature tetragonal phase. Therefore, the cubic phase has to be assumed to have the $Fm\bar{3}m$ space group symmetry (Stockmayer, Stephenson, 1953). Crystal-chemical analysis shows that the shortest, repulsive H...H interactions in the cubic phase favour the disorder: a number of the shortest H...H distances between BH_4^- anions in the disordered $Fm\bar{3}m$ structure is twice smaller than in a hypothetical ordered $F\bar{4}3m$ structure (Stockmayer, Stephenson, 1953). Thus, among the two possible models, the disordered $Fm\bar{3}m$ and the ordered $F\bar{4}3m$, only the first agrees both with crystallographic and thermodynamic data, as well as with the crystal-chemical considerations.

The cubic phase was characterized at 293 K by neutron diffraction on $NaBD_4$ powder (Fischer, Züttel, 2004) and at 200 K by synchrotron diffraction on a $NaBH_4$ single crystal (Filinchuk, Hagemann, 2008). The fully disordered $F\bar{4}3m$ model assumed in the first study is equivalent to the conventional $Fm\bar{3}m$ model used in the second one. The ideal tetrahedral geometry of the borohydride group is defined by the site symmetry for the boron atom. The B−D distance at room temperature is ~1.17 Å, and at 200 K the apparent B−H bond length is 1.09(2) Å. The latter, being corrected for 0.10 Å increment which takes into account the displacement of the electron cloud relative to an average nuclear position of the H-atom (Filinchuk, Hagemann, 2008), makes 1.19 Å.

On cooling below ~190 K or upon compression to ~6 GPa at room temperature a phase with closely related ordered tetragonal structure appears (Kumar, Cornelius, 2005; Sundqvist, Andersson, 2006). Thermal conductivity study allowed to map the *P-T* boundary between the cubic and tetragonal phases at low temperature (Sundqvist, Andersson, 2006). The tetragonal structure was reported in the $P\bar{4}2_1c$ space group (Fischer, Züttel, 2004), but as was pointed out (Filinchuk *et al.*, 2007), it deviates insignificantly from the higher symmetry, and thus can also be described in the space group $P4_2/nmc$. Comparing to the cubic phase, the BH_4 groups in the tetragonal phase are ordered in two different orientations (see Figs. 2a and 2b). As a result, a number of the shortest H...H contacts in the tetragonal phase is reduced by one third comparing to the disordered cubic phase, and the network of the repulsive H...H contacts changes from the isotropic three-dimensional (3D) to the two-dimensional (2D) one, oriented in the *ab* plane. Consequently, the *c*/*a* ratio changes discontinuously upon the cubic-to-tetragonal (c-to-t) transition at ~186 K from 1 to 0.964 (Filinchuk *et al.*, 2008d); this change is more due to the contraction of the *c*-axis than to the expansion in the basal plane. We also found a small but ubrupt volume drop of 0.40% upon the c-to-t transition at ambient pressure. Both discontinuities confirm that the transition is of the first order.

Neutron powder diffraction at 10 K shows that the BD_4 group is neraly ideally tetrahedral and the B−D distance is 1.22 Å (Fischer, Züttel, 2004). High-pressure synchrotron data measured in diamond anvil cells showed that the tetragonal phase can be strongly textured, with its *c*-axis preferentially aligned with the compression direction (Filinchuk *et al.*, 2007).

Above ~9 GPa yet another phase was detected by diffraction and Raman spectroscopy, but both experimental and theoretical efforts originally failed to identify its structure (Kumar, Cornelius, 2005; Araújo *et al.*, 2005). Later its structure has been solved from synchrotron powder diffraction data measured at 11.2 GPa, and it was shown to be of $BaSO_4$ type (Fig. 2c). For the successful solution of the structure, it was absolutely essential to model a texture, including one parameter in the global optimization (Filinchuk *et al.*, 2007). The structure was solved with most *a*-axes approximately aligned with the compression direction. Hydrogen atoms were located as a part of a semi-rigid BH_4 group, with B−H distances of ~1.17 Å. A small volume drop of ~1% was found upon the pressure-induced transition from the tetragonal to the orthorhombic phase (Filinchuk *et al.*, 2007).

In all three structures, Na atoms and BH_4 groups are octahedrally coordinated. In the cubic phase at 200 K Na−B distances are 3.065 Å, in the tetragonal phase at 180 K – 2.976–3.091 Å (Filinchuk *et al.*, 2008d), and in the orthorhombic phase at room temperature and 11.2 GPa – 2.763–2.849 Å.

KBH_4

This substance shows a similar behaviour to $NaBH_4$. Its cubic phase has been studied at room temperature by X-ray diffraction on single crystals (Luck, Schelter, 1999) and by neutron powder diffraction (Renaudin *et al.*, 2004): in both cases it was described in the space group $Fm\bar{3}m$. The cubic phase transforms into a tetragonal one at 65–70 K. Its structure is equivalent to the tetragonal $NaBH_4$, but it was refined in the higher symmetry space group, $P4_2/nmc$. Temperature dependence of the unit cell parameters for both phases has been reported by Renaudin *et al.*, 2004. As the cation's size in the cubic MBH_4 increases, as M goes from Na to K and then to Rb and Cs, the unit cell expands and the shortest H...H distances between the neighbouring BH_4 anions increase. In this way a weaker H...H repulsion in the heavier MBH_4 reduces the temperature of the c-to-t transition. The K−B distance in the cubic KBH_4 is 3.364 Å.

X-ray diffraction on KBH_4 single crystal at 293 K reveals an apparent (uncorrected, for an analysis of corrections see below) B−H distance 1.09(1) Å (Luck, Schelter, 1999). The B−D distance in the tetragonal KBD_4, determined by neutron powder diffraction at 1.5 K, is 1.205(3) Å, and in the cubic structure at 295 K it is 1.196(3) Å (Renaudin *et al.*, 2004). It was shown that the B−D distance in the cubic MBH_4 at 295 K increases as M goes from Na to Cs. Besides the ionic size effect, this may be related to the increased anharmonicity in lighter MBH_4 compared to the heavier MBD_4 (Renaudin *et al.*,

2004), which is presumably related to an increased libration amplitudes for the BH_4 group. The latter would lead to an apparent (illusory) shortening of the B−H bonds.

$Be(BH_4)_2$

The only known $Be(BH_4)_2$ phase was studies by single crystal X-ray diffraction (Marynick, Lipscomb, 1972). Its tetragonal structure contains helical polymeric chains, where the only independent Be cation is coordinated by two bridging borohydride anions (Be−B distances of 2.00 Å) and one terminal borohydride anion (Be−B distance 1.92 Å). It is striking that the therminal BH_4 group is coordinated by the Be atom not via the face but via a tetrahedral edge, just the same way as the bridging BH_4 group. This may be due to the repulsive interaction between hydrogen atoms of the neighbouring BH_4 groups: the corresponding H...H distances (2.24–2.31 Å) are among the shortest known and Be...BH_4 coordination via the tetrahedral face would make these distances even shorter. Be atom has a trigonal-planar environment made by three BH_4 groups, and the bridgind BH_4 group has a linear Be−B−Be geometry. Thus, the low coordination number for the Be atom leads to a reduced dimensionality (1D) of the polymeric structure, where coordination potential of the BH_4 ligands is not fully realized.

The BH_4 groups show slightly deformed tetrahedral geometry with H−B−H angles 104–127°. The apparent (uncorrected) B−H distances fall into the 1.08(2)–1.18(3) Å range at 293 K.

$Mg(BH_4)_2$

As recently reported by two independent groups (Černý *et al.*, 2007; Her *et al.*, 2007), the most stable polymorph has $P6_1$ space group symmetry. In one case (Černý *et al.*, 2007) its structure was solved and refined using combination of synchrotron and neutron powder diffraction data. The synchrotron data contributed most of the information, but the use of neutron data allowed to determinate the orientation of the rigid BH_4 tetrahedra. In the other case (Her *et al.*, 2007), the structure was solved from synchrotron powder data alone, however, only positions of Mg and B atoms were reliably determined. Upon heating above 453 K the hexagonal phase transforms into an orthorhombic one, which remains stable on cooling to room temperature. Its sharp diffraction peaks can be described by an *Immm* structure. However, all peaks were modeled, assuming an antisite disorder, in the 8 times bigger supercell with *Fddd* symmetry (Her *et al.*, 2007).

An intriguing aspect of the $Mg(BH_4)_2$ structures is their complexity. The hexagonal structure contains five symmetry independent Mg^{2+} cations and ten symmetry independent BH_4^- anions. Mg atoms bridged by the BH_4 groups (Mg−Mg 4.6–4.9 Å) form a framework with a novel 3D topology. It contains a variety of 5-membered $(-Mg-BH_4-)_5$ rings that dominate in number over 6- and 8-membered ones, and in this way the structure resembles an amorphous state. The orthorhombic structure contains two symmetry independent Mg^{2+} cations and five symmetry independent BH_4^- anions. Mg atoms bridged by the BH_4 groups (Mg−Mg 4.6–4.7 Å) also form a 3D framework, however the latter does not contain 5-membered rings, but only 4- and 6-membered ones.

On the local level, both phases have the same principles of structural organization. Each Mg atom is surrounded by four BH_4 tetrahedra in a strongly deformed tetrahedral environment, while each BH_4 is nearly linearly coordinated by two Mg cations via the opposite tetrahedral edges. In the hexagonal phase the Mg−B distances vary within the same interval, 2.31–2.53 (Černý *et al.*, 2007) or 2.28–2.57 Å (Her *et al.*, 2007), as in the orthorhombic phase, 2.34–2.47 Å. With respect to the metal-hydrogen bond lengths and coordination geometry for the metal atoms, $Mg(BH_4)_2$ takes an intermediate position between $Be(BH_4)_2$ (flat trigonal coordination by three BH_4 anions) and $LiBH_4$ (nearly ideal tetrahedral coordination by four BH_4 anions). Thus, the ionic metal-to-BH_4 size ratio may be one of the reasons of the high structural complexity of $Mg(BH_4)_2$. Strong distortion of many inequivalent Mg polyhedra provides a sufficient flexibility to meet all the crystal-chemical (*i.e.* energy) requirements: minimization of the repulsive Mg...Mg and H...H interactions, meeting coordination preferences for the BH_4 groups etc.

Since structural complexity is unprecedented for this class of compounds, all known attempts to predict $Mg(BH_4)_2$ structures theoretically were unsuccessful. Geometry optimization of the experimentally determined hexagonal structure, using the density functional theory (DFT), suggests that it has a pseudo or maybe even true $P6_122$ symmetry (Dai *et al.*, 2008).

$Ca(BH_4)_2$

Riktor *et al.*, 2007 reported on existence of several $Ca(BH_4)_2$ phases at different temperatures. Currently several groups are working on structures of these and other phases, and only little has been published till now. Therefore some of the unpublished data available to us are reviewed here too.

For the $Ca(BH_4)_2$ phase, obtained by desolvation of the tetrahydrofurane complex, Miwa *et al.*, 2006 reported an *Fddd* structure. However, analysis of the high-quality synchrotron powder diffraction data revealed that the actual symmetry of this orthorhombic structure is lower (Filinchuk *et al.*, 2008c). Two noncentrosymmetric subgroups of *Fddd*, namely *F*2*dd* and *Fdd*2, provide a much better fit to the experimental data than the centrosymmetric *Fddd* model, and the *F*2*dd* structure has some advantage over the *Fdd*2 one. As shown in the Fig. 3, the arrangement of BH_4 groups in the noncentrosymmetric structure is even simpler than in the *Fddd* model. The structure and symmetry of the orthorhombic phase is maintained from low temperatures up to 495 K. However, as the temperature increases, the cell parameters *a* and *c* continuously approach each other, and at ~495 K a second order transition into a tetragonal $I\bar{4}2d$ phase is taking place (Filinchuk *et al.*, 2008c). The two structures show a group-subgroup relation (index 2). It is important that BH_4 groups are fully ordered in the *F*2*dd* and $I\bar{4}2d$ structures (Figs. 3b and 3c), while tetragonal supergroups of *Fddd* impose a

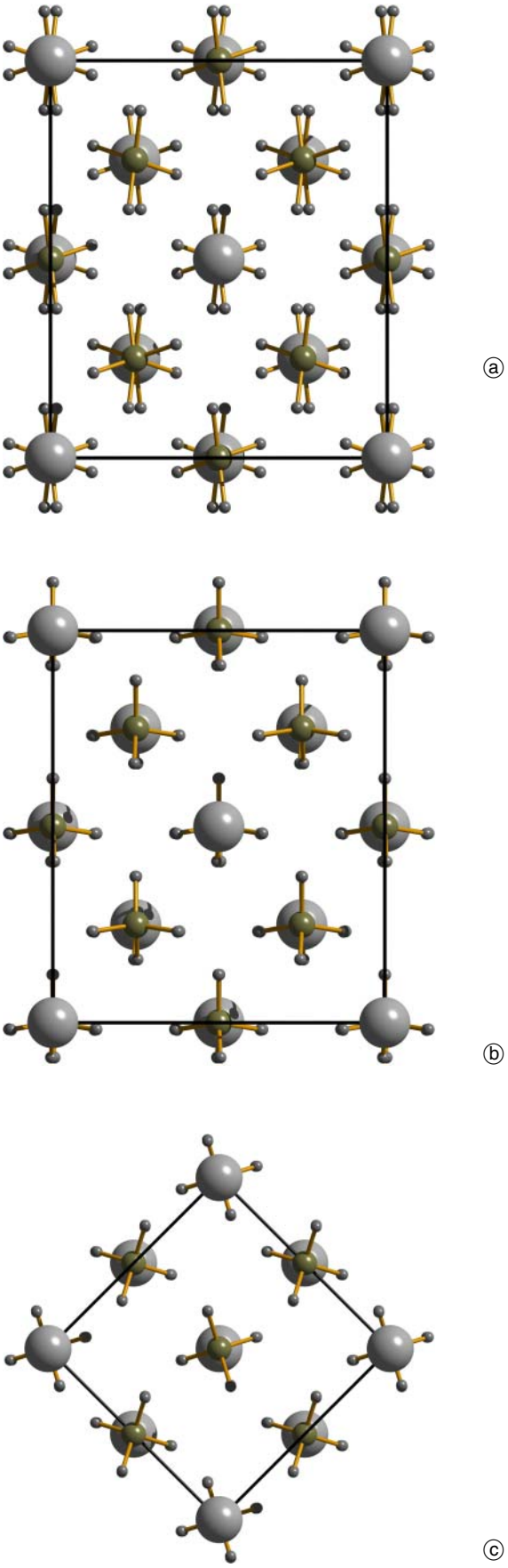

Fig. 3. Crystal structure of the $Ca(BH_4)_2$ phases (Filinchuk *et al.*, 2008c): an *Fddd* model (**a**) and the non-centrosymmetric *F*2*dd* structure (**b**) refined from the same dataset at 91 K; $I\bar{4}2d$ structure after the second order transition $F2dd \rightarrow I\bar{4}2d$ at 495 K (**c**). Big spheres are Ca atoms.

disorder of the borohydride group in a hypothetical $I4_1/amd$ structure.

Above 450 K, the closely related *F*2*dd* and $I\bar{4}2d$ phases transform into a completely different high-temperature phase. Determination of its space group symmetry is ambiguous, and its structure was described in two similar models, namely in space groups $P4_2/m$ (Buchter *et al.*, 2008) and $P\bar{4}$ (Filinchuk *et al.*, 2008c). The high-temperature phase is by 4–6% (depending on temperature) denser than the *F*2*dd* and $I\bar{4}2d$ ones, and it is stable on cooling to room and even to liquid nitrogen temperatures (Filinchuk *et al.*, 2008c). However, Fichtner *et al.* (2008) found that this phase is meta-stable at room temperature, as it slowly transforms back into the orthorhombic phase.

Crystal structures of all three $Ca(BH_4)_2$ phases contain calcium cations nearly octahedrally coordinated by six borohydride anions. Ca–B distances are all within the similar range: 2.82–2.97 Å in the *F*2*dd* phase at 91 K, 2.94–2.98 Å in the $I\bar{4}2d$ phase at 495 K and 2.92–2.94 Å in the $P\bar{4}$ phase at 305 K. For all of the models listed above, the refined geometry of the BH_4^- anions was restrained to an ideal tetrahedral configuration with the B–H bond lengths centered at ~1.17 Å (Filinchuk *et al.*, 2008c). The B–H bond lengths were refined to 1.02(3)–1.16(3) Å for the $P4_2/m$ model (Buchter *et al.*, 2008). In the *Fddd* model (Miwa *et al.*, 2006), the B–H bond lengths and the H–B–H bond angles fall within 1.11–1.13 Å and 102–119°, respectively.

In the *F*2*dd* and $I\bar{4}2d$ structures, Ca atoms form a close-packed diamond-like frameworks where the BH_4 groups have a *T*-shaped coordination. On the contrary, a trigonal-planar arrangement of Ca atoms around BH_4 and 1D chains of Ca atoms are observed in the high-temperature structure.

$Al(BH_4)_3$

At ambient conditions, this substance is liquid. However, two crystalline phases are known at low temperatures, with a transition temperature in the 180–195 K range. Their structures have been studied by single-crystal X-ray diffraction (Aldridge *et al.*, 1997). Each phase is made up of discrete $Al(BH_4)_3$ units, where Al has a trigonal-planar environment with Al–B distances varying in a very narrow interval, 2.10(2)–2.14(2) Å. All BH_4 groups are coordinated by metal atoms via the tetrahedral edges. Locally, the $Al(BH_4)_3$ structures resemble the one for $Be(BH_4)_2$. However, the shortest H...H distances between neighbouring borohydride anions are longer (an average over 2.5 Å) than those in $Be(BH_4)_2$ (2.24–2.31 Å).

The BH_4 anions appear somewhat distorted, partly due to experimental inaccuracies; however these distortions correlate with the results of the electron diffraction studies in the gas phase and *ab initio* calculations (Aldridge *et al.*, 1997). For example, the B–H distances are expected to be longer for the H-atoms coordinated by Al. Indeed, the B–H distances in the B–H...Al bridges are 1.12(3)–1.14(4) Å versus 0.99(4)–1.01(4) Å for the terminal B–H bonds. Note, that the experimental distances are much shorter than the theoretical ones (respectively, 1.27 and 1.19 Å), since they have to be corrected for the displace-

ment of the electron cloud relative to an average nuclear position of the H-atom and for the libration shortening of the B−H bond (Filinchuk, Hagemann, 2008).

Mixed-cation borohydrides

Structures of two mixed-cations borohydrides, $LiK(BH_4)_2$ (Nickels *et al.*, 2008) and $LiSc(BH_4)_4$ (Hagemann *et al.*, 2008), have been studied recently by synchrotron powder diffraction at room temperature. Both compounds are fully stoichiometric, as they do not show statistical occupation of one site by two different cations.

$LiSc(BH_4)_4$ can be described as a complex containing $[Sc(BH_4)_4]^-$ anion (Borisov, Makhaev, 1988), similar to other structurally characterized anion borohydride complexes, such as $(Ph_4P)_2[Mg(BH_4)_4]$ (Makhaev *et al.*, 2004). Sc atoms have a distorted tetrahedral coordination by BH_4 groups, similar to that in $Mg(BH_4)_2$. The borohydride group in $LiSc(BH_4)_4$ was modelled as a rigid body with a common refined B−H distance 1.08 Å (Hagemann *et al.*, 2008).

In $LiK(BH_4)_2$, Li atom is tetrahedrally surrounded by BH_4 groups at Li−B distances 2.51–2.61 Å. An increase of the coordination number for K atom from six in KBH_4 to seven in $LiK(BH_4)_2$ increases also the K−B distances from 3.36 Å to 3.40–3.48 Å. Two independent BH_4 anions are coordinated via the tetrahedral edges. One of them has a typical octahedral coordination (Li_2K_4), similar to that in the cubic MBH_4 phases, while the other shows a new type of coordination – square-pyramidal (Li_2K_2 in the base + K in the apical position). The distortion of the BH_4 anions observed in $LiK(BH_4)_2$ is rather related to experimental inaccuracies than to an influence of the polarizing cations suggested by Nickels *et al.*, 2008, for the discussion on the BH_4 geometry see below.

Discussion and outlook

Geometry of the BH_4 group

Distorted geometry of the BH_4 group in the *Pnma* phase of $LiBH_4$ (Soulié *et al.*, 2002; Züttel *et al.*, 2003), found from early synchrotron powder diffraction experiments, posed a question whether strongly polarizing Li^+ cation can induce deformations of the covalently bonded and therefore presumably rigid tetrahedral BH_4^- anion.

The recent revision of the $LiBH_4$ structures by single crystal synchrotron diffraction (Filinchuk, Chernyshov, 2007; Filinchuk *et al.*, 2008a) showed that the H−B−H angles are nearly the same as in the ideal tetrahedron (109.5°), while three independent B−H bonds have nearly the same lengths. This showed that the BH_4 group is very close to the undistorted tetrahedron and that the spurious distortions are not related to the nature of interaction between X-rays and electron density of light hydrogen atoms. Undistorted geometry of the BH_4 group in $LiBH_4$ was also found from neutron powder diffraction on isotopically substituted $^7Li^{11}BD_4$ (Hartman *et al.*, 2007).

Synchrotron powder diffraction data obtained using a two-dimensional (2D) image plate detector also define the BH_4 anion as nearly ideally tetrahedral (Filinchuk, Chernyshov, 2007; Filinchuk *et al.*, 2008a). An analysis of intensity distributions along the diffraction rings suggests that the powder data obtained with a 1D detector, measuring only a small part of Debye rings, suffers from a poor powder average. Intensity integration over the Debye rings recorded with a 2D detector provides much better average over the grains and therefore higher accuracy of the refined structural parameters. It is therefore crucial in the reliable determination of H-atoms on a small-volume powder sample containing relatively large grains. Considerable deviations from the tetrahedral geometry of the BH_4 group, as for instance recently reported by Nickels *et al.*, 2008 from synchrotron powder diffraction data, should be explained by an experimental inaccuracy. We should note, however, that in certain borohydride structures the BH_4 group can indeed be deformed, provided a good structural reason of this unusual behaviour, such as short H...H contacts, exists (Filinchuk *et al.*, 2008b). Despite it is not observed in $LiBH_4$, an interaction of a strongly polarizing cation with BH_4^- can also lead to deformations, $Al(BH_4)_3$ serves as an example (Aldridge *et al.*, 1997). In any case, such deformation can be reliably detected mainly by diffraction on single crystals or by DFT calculations.

A certain discrepancy exists between the B−H bond lengths determined from X-ray and neutron diffraction experiments. While neutron diffraction at 3.5 K gives the refined B−H distances of 1.208(3)–1.225(6) Å (Hartman *et al.*, 2007), the X-ray diffraction at low temperature yields 1.104(11) to 1.131(15) Å (Filinchuk *et al.*, 2008a). A similar difference has been found from accurate diffraction data on other light hydrides. This difference comes from the well-known displacement of the electron cloud (observed by X-ray diffraction) relative to an average nuclear position (seen by diffraction of neutrons). By its nature, this difference is temperature independent.

Furthermore, DFT calculations find the B−H bond lengths still slightly longer than those from neutron diffraction. This second difference originates from a geometric effect, caused by a libration of the BH_4 unit, which leads to an underestimation of the experimentally determined distances. An extent of the BH_4 libration is not only temperature-dependent (at higher temperature the motion of the BH_4 groups is more pronounced) but also, via frequencies of corresponding phonons, is specific to each crystal structure. The extent of this libration shortening can be estimated from atomic displacement parameters determined from an accurate diffraction experiment.

A combined correction of 0.10 Å has been recently suggested from the analysis of the available structural data for $NaBH_4$ and its hydrate at low temperatures (Filinchuk, Hagemann, 2008). It roughly accounts both for the displacement of the electron cloud on H-atoms and the effect of libration observed in ordered structures at 200–300 K. Displacement of H-atoms from B along the B−H bonds brings positions of hydrogen atoms determined from X-ray diffraction in agreement with theoretically predicted values.

The two corrections were evaluated separately from synchrotron diffraction data collected on $LiBH_4$ single crystals. It is shown (Filinchuk *et al.*, 2008a) that the dis-

placement of the electron cloud from the nuclear position of H-atoms contributes ~0.08 Å to the apparent shortening of the B−H bonds. The libration correction in the *Pnma* phase at 225 K was estimated to be 0.034 Å, while in the high-temperature phase at 535 K it is much bigger, ~0.10 Å.

In is interesting to note here that the libration amplitudes for the BH_4 group, along with the related anharmonicities, are larger than for the heavier BD_4. Consequently, the cell parameters for MBH_4 are slightly larger (usually by less than 1% of the cell volume, Renaudin *et al.*, 2004) than those for MBD_4. The different contribution of H and D to the libration correction should also be considered in accurate comparisons of interatomic distances.

Correction of H-positions determined from X-ray diffraction for systematic errors leads to an increased accuracy of this technique applied to low-Z hydride systems. It also allows to compare directly the results obtained by different diffraction techniques and by theoretical calculations. Making comparisons without applying proper systematic corrections has lead to some odd conclusions (Chater *et al.*, 2006; Siegel *et al.*, 2007; Yang *et al.*, 2007; Wu *et al.*, 2008), when neutron powder diffraction giving irregular BH_4 groups was considered more accurate than singe crystal X-ray diffraction yielding ideally tetrahedral BH_4 groups. When the corrections are applied, we arrive to the opposite conclusion. Indeed, nonoverlapped three-dimensional information uncovered by the scattering of X-rays on single-crystals gives an advantage over the neutron powder diffraction, where all scattering is projected on one dimension.

BH_4...M and BH_4...BH_4 contacts

Coordination number (CN) for metal atoms increases with their ionic radii. For Be and Al atoms CN = 3 (trigonal-planar coordination by three BH_4 group), for Mg atoms CN = 4 (deformed tetrahedral coordination), for Li atoms at ambient and moderate pressures CN = 4 (tetrahedral coordination), but at higher pressure CN increases to 6 (octahedral coordination). For the largest Na, K and Ca atoms CN = 6 and the coordination is ideal or deformed octahedral. Potassium atom in $LiK(BH_4)_2$ is seven-coordinated, its coordination environment is a capped trigonal prism.

Coordination number for the borohydride anion changes along with $M(BH_4)_n$ shoichiometry. At $n = 1$, the typical coordination geometries are tetrahedral (ambient pressure phases of $LiBH_4$, $LiK(BH_4)_2$) and octahedral (cubic $LiBH_4$, $NaBH_4$, KBH_4 and $LiK(BH_4)_2$). As n increases, low-connected *T*-shaped ($Ca(BH_4)_2$) and linear ($Be(BH_4)_2$ and $Mg(BH_4)_2$) geometries occur, and in the structures with low dimensionalities ($Be(BH_4)_2$ and $Al(BH_4)_3$) the BH_4 group can be coordinated even by only one metal atom. Unusual coordination geometries for the BH_4 group are square-planar, found in the *Ama*2 phase of $LiBH_4$, and square-pyramidal in $LiK(BH_4)_2$.

The diversity of coordination geometries for the BH_4^- anion indicates that it behaves as a flexible ligand, adjusting to the requirements (CN) of the metal atom. However, the BH_4...M interaction shows a very directional behaviour. As a rule, the borohydride groups are connected to metal atoms via the tetrahedral edges. The exceptions are the hexagonal phase of $LiBH_4$, where the BH_4 group is coordinated via all four tetrahedral faces, and the shortest Li−B contact (2.37 Å) in the *Pnma* phase of $LiBH_4$, where the borohydride group is coordinated by Li atom also via the face. Coordination via vertices was observed only in some $Ca(BH_4)_2$ structures (Filinchuk *et al.*, 2008c). Directional coordination of the BH_4 group by metal atoms clearly indicates non-spherical nature of the BH_4 anion, which has geometrical and possibly also electronic preferences in BH_4...M interaction.

The H...H distances between neighbouring BH_4 groups exceed 2.2 Å, and in most cases they are even longer. The only exception is the *Ama*2 phase of $LiBH_4$, where at rather low pressure of 2.4 GPa a strikingly short H...H contact between adjacent BH_4 anions has been found (1.92 Å in the experimental structure and 1.87 Å in the theoretically optimized model). It was shown that the short H...H interaction distorts the BH_4 anion, and this is likely to decrease the activation energy for hydrogen desorption. It was suggested that the internal pressure in the $LiBH_4$ structure may be tuned by a partial substitution of lithium by larger cations, or substitution of some BH_4 groups by bigger anions (Filinchuk *et al.*, 2008b). The resulting $LiBH_4$-based substance with *Ama*2 structure may show more favourable hydrogen storage properties than pure $LiBH_4$ and may turn out to be useful for hydrogen storage applications.

Chemically destabilized borohydrides?

Substitution of metal atoms or BH_4 groups by other cations and anions can be considered as a way to alter stability of borohydrides.

Two mixed-cations borohydrides have been found recently: $LiK(BH_4)_2$ (Nickels *et al.*, 2008) and $LiSc(BH_4)_4$ (Hagemann *et al.*, 2008). However, hydrogen desorption temperature for such compounds appears not to be lower than for the single cation constituents, but merely intermediate between the two (Nickels *et al.*, 2008).

Notably, mixed-anion derivatives show more favourable hydrogen storage properties than the individual components; this is well illustrated for the $LiBH_4$−$LiNH_2$ system (Meisner *et al.*, 2006). Currently, two mixed borohydride-amide phases have been structurally characterized: $Li_4(BH_4)(NH_2)_3$ (Filinchuk *et al.*, 2006; Chater *et al.*, 2006) and $Li_2(BH_4)(NH_2)$ (Chater *et al.*, 2007). Very recently an existence of mixed borohydrides-alanates has been reported: $Na_4(BH_4)(AlH_4)_3$ crystallizes in a primitive cubic $2 \times 2 \times 2$ supercell of $NaBH_4$ (Smith *et al.*, 2007), $Mg(BH_4)(AlH_4)$ was identified with yet unknown crystal structure (Zhao *et al.*, 2007). Hydrogen desorption properties for the latter class of compounds are not yet reported. Currently, only amide containing mixed-anion derivatives showed some decreasing of the hydrogen evolution temperature (Meisner *et al.*, 2006). However, we can see that the mixed-anion derivatives show a bigger improvement of hydrogen storage properties than the mixed-cation ones. This may be partly due to the formation of dihydrogen bonds (such as B−H...H−N) between different anions, which are expected to facilitate hydrogen desorption. A

similar modification of light metal borohydrides can be achieved by introducing neutral hydrogen-rich molecules, such as ammonia or water. Such examples include $Mg(BH_4)_2 \cdot 2\,NH_3$ (Soloveichik *et al.*, 2008) and $NaBH_4 \cdot 2\,H_2O$ (Filinchuk, Hagemann, 2008); the first substance shows very favourable hydrogen storage properties.

All the known structures of the borohydride derivatives are fully ordered and shoichiometric, without statistical occupation of cation or anion sites. The first and currently the only system where a gradual replacement of BH_4 has been found is $LiBH_4$ + LiCl, where chloride anions partially replace borohydride anions at elevated temperatures (Mosegaard *et al.*, 2008). Comparison of the unit cell volumes for different inorganic salts suggests that the size of anions change according to the sequence $I^- > BH_4^- > Br^- > Cl^-$ (Filinchuk, Hagemann, 2008). This variety gives an efficient tool to tune the unit cell volume and internal lattice pressure of borohydrides. We suggest that a partial substitution of the BH_4 group by halide anions (Hal) would possibly open the way to modify metal borohydrides and influence their structural stability, in particular to obtain high-pressure polymorphs of $LiBH_4$ at ambient conditions (Filinchuk *et al.*, 2008a). *In-situ* powder diffraction study of the reaction mixtures at variable temperature should be used to probe different $M(BH_4)_n$ + M′Hal combinations.

A final note on a possible modification of the BH_4 group is warranted. A partial substitution of hydrogen atoms by fluorine atoms has been achieved in alanates, showing that the complex hydride $Na_3AlH_{6-x}F_x$ is less stable than Na_3AlH_6 (Brinks *et al.*, 2008). Due to the high stability of the covalent B−H bond, a similar chemical modification of the BH_4 anion is unlikely. We note, however, that amidoboranes, a new class of high-capacity hydrogen storage materials of the general formula $M(BH_3NH_2)_n$ (Xiong *et al.*, 2007), can be considered as modified borohydrides, where one hydrogen atom in BH_4^- has been exchanged for NH_2. Nevertheless, amidoboranes were currently obtained not by modifying borohydrides but from ammonia-borane, which contains the ready-made B−N bond.

Diffraction studies of stability regions and structure evolution with external stimuli

It was shown above that powder diffraction can provide accurate information about structure of borohydrides. In some of the best examples, its accuracy is comparable to the one of the single crystal diffraction. However, a profound use of this technique is to study structure evolution under variable pressure or temperature. Bulk modulus and coefficients of thermal expansion, together with information on the symmetry and structure, provide the basis for validation of theoretical models. A study of structure evolution with external stimuli thus appears to be an essential step before starting any theoretical calculations.

$LiBH_4$ serves as an illustration of the complex behaviour (Filinchuk *et al.*, 2008a). While the high-temperature hexagonal phase shows a uniform and isotropic temperature expansion, the low-temperature *Pnma* phase reveals non-linear and highly anisotropic behaviour (Fig. 4). The

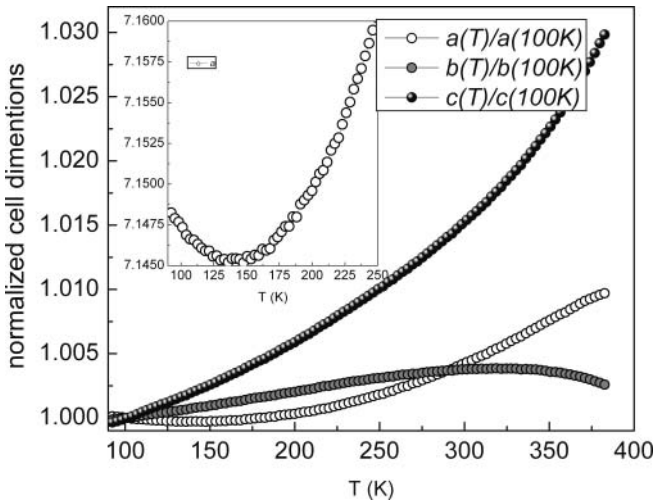

Fig. 4. Cell dimensions of the *Pnma* phase of $LiBH_4$ as a function of temperature (Filinchuk *et al.*, 2008a), scaled to the experimental values at 100 K. The low-temperature behaviour of the *a* parameter is shown in the inset.

cell dimension *b* continuously contracts on heating from 300 K to the transition temperature. Such thermal expansion reflects an anharmonicity of the potential of the crystal binding, which should be taken into account in theoretical models. It is remarkable that the thermal expansion is also anomalous at low temperatures: the parameter *a* deviates from linear dependence below 200 K, shows a minimum at ∼150 K, and then increases on cooling. This observation can be related to a thermodynamic bistability involving the high-pressure *Ama*2 phase. Indeed, according to thermal conductivity measurements at high pressures, the free energy of $LiBH_4$ below 180 K and ambient pressure should have two minima (Talyzin *et al.*, 2007). It is remarkable that the thermal expansion in the *a*-direction deviates from the linear behaviour in the same temperature range.

The need to consider high-pressure phases while explaining the temperature behaviour of $LiBH_4$ calls for a combined pressure-temperature (*P-T*) study of the corresponding phase diagram. *In situ* synchrotron diffraction serves as a best probe to map the *P-T* diagram (Fig. 5), identify the phases and follow their structural evolution (Dmitriev *et al.*, 2008). Such diagram, with all supporting information, allows to evaluate fundamental thermody-

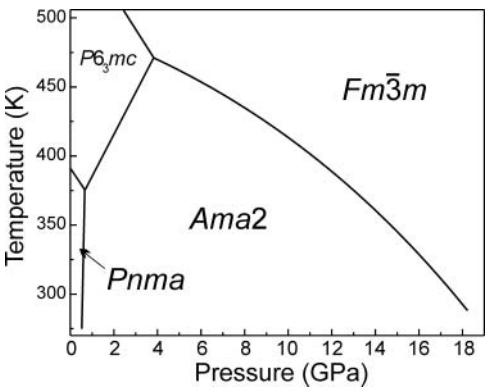

Fig. 5. Pressure-temperature phase diagram of $LiBH_4$ from synchrotron diffraction experiments (Dmitriev *et al.*, 2008).

namic and structural properties of $LiBH_4$ and may guide a rational chemical modification of $LiBH_4$. A pressure behaviour of the transition temperature allows to estimate an entropy change on the corresponding transition (Pistorius, 1974), and thus to draw a conclusion about its mechanism. An analysis of symmetry changes and structural deformations, followed by a group theoretical analysis, yields a unified picture of the phase transformations in $LiBH_4$. The results are shortly presented below.

Phenomenological and crystal-chemical analysis of mechanisms of phase transitions

An existence of cation-anion layers in all four $LiBH_4$ phases is suggested from the phenomenological analysis of mechanisms of phase transitions (Dmitriev *et al.*, 2008). This conclusion is not trivial from purely geometrical point of view, but it can find a rational explanation considering the experimentally determined structures. A clear evidence for the existence of cation-anion layers is found in the hexagonal phase, where BH_4 tetrahedron has three short B . . . Li contacts in the *ab* plane and a long one along the *c* axis. In the *Pnma* phase, these layers are corrugated and the structure is less anisotropic. In the high-pressure phases the existence of cation-anion layers is less obvious. However, the layers where Li and BH_4 groups are associated by means of the shorter B . . . Li contacts can be identified in the (011) plane of the *Ama*2 structure. Due to the high symmetry of the cubic structure different hypothetical layers can be identified there. However, only one type of layers is consistent both with geometrical considerations and with the phenomenological model: these are cation-anion layers situated in the (111) plane, very similar to those found in the hexagonal phase.

Clearly, the formation of layers in the $LiBH_4$ structures is not determined by coordination polyhedra for Li and BH_4 groups, since corresponding coordination numbers and geometries vary with pressure and temperature. However, directional coordination of the BH_4 group by Li atoms clearly indicates geometrical and possibly also electronic preferences of BH_4 . . . M interaction. Interaction of non-spherical BH_4 anions with spherical Li cations results in cation-anions layers, which determine the mechanisms of transitions between polymorphic structures. Directional interaction of tetrahedral BH_4 with spherical metal atoms explains the relative complexity of $LiBH_4$ structures and of the *P-T* phase diagram in comparison with NaCl, where both cation and anion are spherical.

Destabilization of borohydrides upon phase transitions

Another application of combined crystal-chemical and phenomenological analysis of polymorphic transitions would be to reveal destabilization of borohydrides upon phase transitions, achieved via formation of short H . . . H distances and deformation of tetrahedral BH_4 anions. A sign of such destabilization was observed in the *Ama*2 phase of $LiBH_4$ (Filinchuk *et al.*, 2008b). A similar destabilization in $LiBH_4$ or similar systems may be achieved during reconstructive phase transitions or melting. Indeed, some hydrogen desorption from $LiBH_4$ occurs upon the transition from *Pnma* to $P6_3mc$ phase and on melting (Mauron *et al.*, 2008). It is suggested (Dmitriev *et al.*, 2008) that other phase boundaries in the *P-T* phase diagram of pure or chemically modified $LiBH_4$ should be addressed with respect to a possible hydrogen desorption. Chemical modification of $LiBH_4$, for example by exchanging a part of BH_4 anions by halide anions (Mosegaard *et al.*, 2008), can be used along with pressure and temperature to investigate hydrogen desorption properties of modified $LiBH_4$ within the given *P-T* phase diagram.

Note added in proof

While this review was in press, a single crystal synchrotron diffraction study of the hexagonal $Mg(BH_4)_2$ revealed that its actual symmetry is not $P6_1$ but $P6_122$ (Filinchuk, Y.; Černý, R.; Hagemann, H.: An insight into $Mg(BH_4)_2$ with synchrotron X-ray diffraction: structure revision, crystal chemistry and anomalous thermal expansion. (2008), submitted.), in agreement with theoretical suggestion by Dai *et al.*, 2008.

References

Aldridge, S.; Blake, A. J.; Downs, A. J.; Gould, R. O.; Parsons, S.; Pulham, C. R.: Some tetrahydroborate derivatives of aluminium: crystal structures of dimethylaluminium tetrahydroborate and the α and β phases of aluminium tris(tetrahydroborate) at low temperature. J. Chem. Soc., Dalton Trans. (1997) 1007-1012.

Araújo, C. M.; Ahuja, R.; Talyzin, A. V.; Sundqvist, B.: Pressure-induced structural phase transition in $NaBH_4$. Phys. Rev. B. **72** (2005) 054125.

Borisov, A. P.; Makhaev, V. D.: Anion borohydride complexes of scandium, titanium and vanadium with organic cations. Russ. J. Inorg. Chem. **33** (1988) 3030-3035.

Brinks, H. W.; Fossdal, A.; Hauback, B. C.: Adjustment of the stability of complex hydrides by anion substitution. J. Phys. Chem. C. **112** (2008) 5658-5661.

Buchter, F.; Łodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Mauron, Ph.; Züttel, A.; Sheptyakov, D.; Barkhordarian, G.; Bormann, R.; Chłopek, K.; Fichtner, M.; Sørby, M.; Riktor, M.; Hauback, B.; Orimo, S.: Structure of $Ca(BD_4)_2$ β-phase from combined neutron and synchrotron X-ray powder diffraction data and density functional calculations. J. Phys. Chem. B. **112** (2008) 8042-8048.

Černý, R.; Filinchuk, Y.; Hagemann, H.; Yvon K.: Magnesium borohydride: synthesis and crystal structure. Angew. Chem. Int. Ed. **46** (2007) 5765-5767.

Chater, P. A.; David, W. I. F.; Johnson, S. R.; Edwards, P. P.; Anderson, P. A.: Synthesis and crystal structure of $Li_4BH_4(NH_2)_3$. Chem. Commun. (2006) 2439-2441.

Chater, P. A.; David, W. I. F.; Anderson, P. A.: Synthesis and structure of the new complex hydride $Li_2BH_4NH_2$. Chem. Commun. (2007) 4770-4772.

Dai, B.; Sholl, D. S.; Johnson, J. K.: First-principles study of experimental and hypothetical $Mg(BH_4)_2$ crystal structures. J. Phys. Chem. C. **112** (2008) 4391-4395.

Dmitriev, V.; Filinchuk, Y.; Chernyshov, D.; Talyzin, A.; Dzwilewski, A.; Andersson, O.; Sundqvist, B.; Kurnosov, A.: Pressure-temperature phase diagram of $LiBH_4$: synchrotron x-ray diffraction experiments and theoretical analysis. Phys. Rev. B. **77** (2008) 174112.

Fichtner, M.; Chłopek, K.; Longhini, M.; Hagemann H.: Vibrational spectra of $Ca(BH_4)_2$. J. Phys. Chem. C. **112** (2008) 11575-11579.

Filinchuk, Y. E.; Yvon, K.; Meisner, G. P.; Pinkerton, F. E.; Balogh, M. P.: On the composition and crystal structure of the new quaternary hydride phase $Li_4BN_3H_{10}$. Inorg. Chem. **45** (2006) 1433-1435.

Filinchuk, Y.; Chernyshov, D.: Looking at hydrogen atoms with X-rays: comprehensive synchrotron diffraction study of $LiBH_4$. Acta Cryst. A. **63** (2007) s240.

Filinchuk, Y.; Talyzin, A.; Chernyshov, D.; Dmitriev, V.: High-pressure phase of $NaBH_4$: crystal structure from synchrotron powder diffraction data. Phys. Rev. B. **76** (2007) 092104.

Filinchuk, Y.; Chernyshov, D.; Černý, R.: The lightest borohydride probed by synchrotron diffraction: experiment calls for a new theoretical revision. (2008a) J. Phys. Chem. C. **112** (2008) 10579-10584.

Filinchuk, Y.; Chernyshov, D.; Nevidomskyy, A.; Dmitriev, V.: High-pressure polymorphism as a step towards destabilization of $LiBH_4$. Angew. Chem. Int. Ed. **47** (2008b) 529-532.

Filinchuk, Y.; Rönnebro, E.; Chandra, D.: Crystal structures and phase transformations in $Ca(BH_4)_2$. Acta Mater. (2008c) DOI: 10.1016/j.actamat.2008.10.034.

Filinchuk, Y.; Chernyshov, D.; Dmitriev, V.: (2008d) unpublished results.

Filinchuk, Y.; Hagemann, H.: Structure and properties of $NaBH_4 \cdot 2H_2O$ and $NaBH_4$. Eur. J. Inorg. Chem. (2008) 3127-3133.

Fischer, P.; Züttel, A.: Order-disorder phase transition in $NaBD_4$. Mater. Sci. Forum. **443-444** (2004) 287-290.

Grochala, W.; Edwards, P. P.: Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen. Chem. Rev. **104** (2004) 1283-1315.

Hagemann, H.; Longhini, M.; Kaminski, J. W.; Wesolowski, T. A.; Černý, R.; Penin, N.; Sørby, M. H.; Hauback, B. C.; Severa, G.; Jensen, C. M.: $LiSc(BH_4)_4$: a novel salt of Li^+ and discrete $Sc(BH_4)_4^-$ complex anions. J. Phys. Chem. A **112** (2008) 7551-7555.

Hartman, M. R.; Rush, J. J.; Udovic, T. J.; Bowman, R. C. Jr.; Hwang, S. J.: Structure and vibrational dynamics of isotopically labeled lithium borohydride using neutron diffraction and spectroscopy. J. Solid State Chem. **180** (2007) 1298-1305.

Her, J.-H.; Stephens, P. W.; Gao, Y.; Soloveichik, G. L.; Rijssenbeek, J.; Andrus, M.; Zhao, J.-C.: Structure of unsolvated magnesium borohydride $Mg(BH_4)_2$. Acta Cryst. B. **63** (2007) 561-568.

Johnston, L.; Hallett, N. C.: Low temperature heat capacities of inorganic solids. XIV. Heat capacity of sodium borohydride from 15-300°K. J. Am. Chem. Soc. **75** (1953) 1467-1468.

Kumar, R. S.; Cornelius, A. L.: Structural transitions in $NaBH_4$ under pressure. Appl. Phys. Lett. **87** (2005) 261916.

Luck, R. L.; Schelter, E. J.: Potassium borohydride. Acta Cryst. C. **55** (1999) IUC9900151.

Makhaev, V. D.; Borisov, A. P.; Antsyshkina, A. S.; Sadikov, G. G.: Synthesis and properties of new magnesium tetrahydroborate complexes: the crystal structure of $(Ph_4P)_2[Mg(BH_4)_4]$. Russ. J. Inorg. Chem. **49** (2004) 323-330.

Marynick, D. S.; Lipscomb, W. N.: Crystal structure of beryllium borohydride. Inorg. Chem. **11** (1972) 820-823.

Mauron, P.; Buchter, F.; Friedrichs, O.; Remhof, A.; Bielmann, M.; Zwicky, C. N.; Zuttel, A.: Stability and reversibility of $LiBH_4$. J. Phys. Chem. B. **112** (2008) 906-910.

Meisner, G. P.; Scullin, M. L.; Balogh, M. P.; Pinkerton, F. E.; Meyer, M. S.: Hydrogen release from mixtures of lithium borohydride and lithium amide: a phase diagram study. J. Phys. Chem. B. **110** (2006) 4186-4192.

Miwa, K.; Aoki, M.; Noritake, T.; Ohba, N.; Nakamori, Y.; Towata, S.-i.; Züttel, A.; Orimo, S.-i.: Thermodynamical stability of calcium borohydride $Ca(BH_4)_2$. Phys. Rev. B. **74** (2006) 155122.

Mosegaard, L.; Moeller, B.; Jorgensen, J.-E.; Filinchuk, Y.; Cerenius, Y.; Hanson, J.; Dimasi, E.; Besenbacher, F.; Jensen, T.: Reactivity of $LiBH_4$: in-situ synchrotron radiation powder X-ray diffraction study. J. Phys. Chem. C. **112** (2008) 1299-1303.

Nickels, E. A.; Jones, M. O.; David, W. I. F.; Johnson, S. R.; Lowton, R. L.; Sommariva, M.; Edwards, P. P.: Tuning the decomposition temperature in complex hydrides: synthesis of a mixed alkali metal borohydride. Angew. Chem. Int. Ed. **47** (2008) 2817-2819.

Talyzin, A. V.; Andersson, O.; Sundqvist, B.; Kurnosov, A.; Dubrovinsky, L.: High-pressure phase transition in $LiBH_4$. J. Solid State Chem. **180** (2007) 510-517.

Orimo, S.-i.; Nakamori, Y.; Eliseo, J. R.; Züttel, A.; Jensen, C. M.: Complex hydrides for hydrogen storage. Chem. Rev. **107** (2007) 4111-4132.

Pistorius, C. W. F. T.: Melting and polymorphism of $LiBH_4$ to 45 kbar. Z. Phys. Chem. Neue Folge. **88** (1974) 253-263.

Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K.: Structural and spectroscopic studies on the alkali borohydrides MBH_4 (M = Na, K, Rb, Cs). J. Alloys Compd. **375** (2004) 98–106.

Riktor, M. D.; Sørby, M. H.; Chłopek, K.; Fichtner, M.; Buchter, F.; Züttel, A.; Hauback, B. C.: In situ synchrotron diffraction studies of phase transitions and thermal decomposition of $Mg(BH_4)_2$ and $Ca(BH_4)_2$. J. Mater. Chem. **17** (2007) 4939–4942.

Siegel, D. J.; Wolverton, C.; Ozoliņs, V.: Reaction energetics and crystal structure of $Li_4BN_3H_{10}$ from first principles. Phys. Rev. B. **75** (2007) 014101.

Soloveichik, G.: Metal borohydrides as hydrogen storage materials. Material Matters (Aldrich). **2**. No.2 (2007) 11–14.

Soloveichik, G.; Her, J.-H.; Stephens, P. W.; Gao, Y.; Rijssenbeek, J.; Andrus, M.; Zhao, J.-C.: Ammine magnesium borohydride complex as a new material for hydrogen storage: structure and properties of $Mg(BH_4)_2 \cdot 2NH_3$. Inorg. Chem. **47** (2008) 4290–4298.

Soulié, J.-P.; Renaudin, G.; Černý, R.; Yvon, K.: Lithium boro-hydride $LiBH_4$. I. Crystal structure. J. Alloys Compd. **346** (2002) 200–205.

Smith, Ch. I.; Jones, M. O.; Johnson, S. R.; David, W. I. F.; Edwards, P. P.: Mixed borohydride-alanates as potential hydrogen storage materials. Abstract in ISHE, International symposium on materials issues in a hydrogen economy. Richmond, Virginia. (2007) W32.

Stockmayer, W. H.; Stephenson, C. C.: The nature of the gradual transition in sodium borohydride. J. Chem. Phys. **21** (1953) 1311–1312.

Sundqvist, B.; Andersson, O.: Low-temperature phase transformation in $NaBH_4$ under pressure. Phys. Rev. B. **73** (2006) 092102.

Wu, H.; Zhou, W.; Udovic, T. J.; Rush, J. J.; Yildrim, T.: Structures and crystal chemistry of Li_2BNH_6 and $Li_4BN_3H_{10}$. Chem. Mater. **20** (2008) 1245–1247.

Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F.: High-capacity hydrogen storage in lithium and sodium amidoboranes. Nature Mat. **7** (2007) 138–141.

Yang, J. B.; Wang, X. J.; Cai, Q.; Yelon, W. B.; James, W. J.: Crystal and electronic structures of the complex hydride $Li_4BN_3H_{10}$. J. Appl. Phys. **102** (2007) 033507.

Zhao, J.-C.; Cui, J.; Gao, Y.; Kniajansky, S.; Lemmon, J.; Raber, T.; Rijssenbeek, J.; Rubinsztajn, M.; Soloveichik, G.: GE Progress within the DOE Metal Hydride Center of Excellence for Hydrogen Storage. DOE Annual Progress Report. (2007) 370–374.

Züttel, A.; Rentsch, S.; Fischer, P.; Wenger, P.; Sudan, P.; Mauron, Ph.; Emmenegger, Ch.: Hydrogen storage properties of $LiBH_4$. J. Alloys Compd. **356–357** (2003) 515–520.

Züttel, A.; Borgschulte, A.; Orimo, S.-i.: Tetrahydroborates as new hydrogen storage materials. Scripta Mater. **56** (2007) 823–828.