Pressure-induced phase of NaAlH$_4$: A potential candidate for hydrogen storage?

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The electronic structure and structural stability of the technologically interesting material NaAlH$_4$ are studied using an $ab$ initio projected augmented plane-wave method for different possible structure modifications. We predict that $\alpha$-NaAlH$_4$ converts to $\beta$-NaAlH$_4$ at 6.43 GPa with a 4 $%$ volume contraction. Both modifications have nonmetallic character with finite energy gaps, the calculated band gap for $\beta$-NaAlH$_4$ being almost half of that for the $\alpha$ phase. $\beta$-NaAlH$_4$ stores hydrogen more volume efficient than the $\alpha$ phase and would if stabilized at ambient conditions be an interesting candidate for further studies with regard to hydrogen absorption/desorption efficiency. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566086]

Introduction of “hydrogen economy” requires safe and efficient storage of hydrogen, and hence, potential solid storage materials have been intensively studied for several decades. The hitherto known hydrides with high capacity for hydrogen absorption/desorption, such as NaAlH$_4$, MgH$_2$, and LiH have a high relatively H content (7–13 wt $%)$, but owing to the presence of strong ionic/covalent bonding interactions, the desorption temperature is high ($>250{°}C$). In contrast, MgH$_2$ and LiH have a high relatively H content (7–13 wt $%)$, but owing to the presence of strong ionic/covalent bonding interactions, the desorption temperature is high ($>250{°}C$). In the search for suitable materials for reversible hydrogen storage, alkali aluminum hydrides such as NaAlH$_4$ and LiAlH$_4$ have attracted interest mainly due to the high relative weight of stored hydrogen (7.5 and 10.6 wt $%$, respectively). Recently Bogdanovic and co-workers$^{8,9}$ have established that sodium aluminum hydrides, which were earlier considered in actual practice as irreversible with respect to hydrogen absorption/desorption, could be made reversible by doping with Ti. Efforts$^{5,6}$ have also been made to improve the hydrogen reversibility of NaAlH$_4$ by ball milling in combination with (or without) additives. In line with this, considerable interest is attached to the structural properties of NaAlH$_4$ at higher pressures, but no experimental or theoretical high-pressure studies have hitherto been performed. A theoretical investigation of NaAlH$_4$ is also of topical interest because of the difficulties involved in establishing the location of the hydrogen atoms by high-pressure diffraction techniques.

At ambient conditions NaAlH$_4$ crystallizes in the tetragonal structure$^{5,8}$ shown in Fig. 1(a) (space group $I4_1/a$). The $[\text{AlH}_4]^-$ anion has a compressed tetrahedral geometry with Al–H distances of 1.603 Å. The Na$^+$ cation has eight nearest H neighbors which define the vertices of a distorted triangular dodecahedron. Related compounds with the same stoichiometry take rather different structures: LiBH$_4$ (hexagonal-P6$_3$m*c),$^{9}$ NaGaH$_4$ (orthorhombic-Cmc2$_1$),$^{10}$ NaBH$_4$ (cubic-Fm3m),$^{11}$ LiAlH$_4$ (monoclinic-P2$_1$/$c$),$^{12}$ KGaH$_4$ (orthorhombic-Pnma),$^{13}$ and SrMgH$_4$ (orthorhombic-Cmc2$_1$).$^{14}$ The present theoretical study includes the actually established structure for NaAlH$_4$ as well as the just mentioned six potential alternatives.

Total energies have been calculated by the projected augmented plane-wave$^{15}$ implementation of the Vienna $ab$ initio simulation package.$^{16}$ The generalized gradient approximation$^{17}$ were used to obtain accurate exchange and correlation energies for a particular ionic configuration. The structures are fully relaxed for all volumes considered in the present study using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. For the tetragonal NaAlH$_4$ structure we used 432 $k$ points in the whole Brilouin zone. A similar density of $k$ points was used for the other structures. In order to avoid ambiguities regarding the free-energy results we have used the same energy cutoff and similar $k$-grid densities in all calculations. At least 0.01 meV/atom was placed as a criterion on the self-consistent conver-

![FIG. 1. Crystal structure of (a) $\alpha$-(tetragonal-$I4_1/a$) and (b) $\beta$-NaAlH$_4$ (SrMgH$_4$-type; orthorhombic-Cmc2$_1$).]

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The energetics of the total energy, and the calculations reported here used a plane wave cutoff of 600 eV. The zero-point entropy contribution to the free energy has not been included in the calculations, but its contribution should in any case be very small and should not affect transition pressures significantly.18 A similar approach was successfully applied in the case of MgH2, where the three experimentally observed high-pressure phases where reproduced rather well.19

In agreement with the experimental findings,20 the actual tetragonal structure takes the lowest energy (Fig. 2) among the seven considered phases. Hence, at ambient conditions NaAlH4 crystallizes in the tetragonal structure (hereafter named as the α phase) with lattice constants a = 4.9965 Å and c = 11.0828 Å, [close (within 1 %) to the low-temperature (8 K) experimental values8 of a = 4.9801 and c = 11.1483 Å]. Similarly the calculated atomic coordinates for α-NaAlH4 are in good agreement with experimental findings (Table I). At higher pressures, α-NaAlH4 transforms to an orthorhombic SrMgH4-type structure (space group $Cmcm$ [Figs. 1(b) and 2]), hereafter β-NaAlH4. The coordination number (CN) of Al changes from 4 in α-NaAlH4 to 6 in the β phase, viz., consistent with the expected general trend of increasing CN with weakening of the covalent/ionic bonding with increasing pressure. We have calculated the total energy as a function of unit-cell volume for 12 different volumes and fitted the results to the so-called universal equation state20 and thus obtained bulk moduli ($B_0$) and pressure derivatives ($B_0^\prime$) for α- and β-NaAlH4. Both phases have low bulk moduli ($B_0$ = 19.3 and 36.5 GPa; $B_0^\prime$ = 4.77 and 3.78, respectively) implying that NaAlH4 is a very soft and easily compressible material. $B_0$ for β-NaAlH4 is almost twice that of the α phase, largely due to the increased CN and the lower equilibrium volume of β-NaAlH4.

The theoretically generated pressure-volume curve (Fig. 3) shows that α-NaAlH4 is converted into the β phase at 6.43 GPa with a volume reduction of ~ 4 %. In order to obtain a clearer picture of the conditions at the transition point and the possibility for formation of the β phase, we show the pressure dependence of the Gibbs free energy difference ($\Delta G$) between the α- and β-NaAlH4 in the inset to Fig. 3. The calculated total-energy difference (Fig. 2) between the two structures at their equilibrium volumes is only 126 meV/f.u. (12.2 kJ/mol). The equilibrium volume of β-NaAlH4 at 1 bar is 9% smaller than that of the α phase (see Fig. 2), indicating that hydrogen can be stored more efficiently in the β phase. At higher pressures the involved energy difference between α- and β-NaAlH4 is small. In line with the findings for TiO2,21 one should search for possibilities to stabilize the high-pressure phase β-NaAlH4 at ambient pressure by appropriate treatment (perhaps by chemical means, that moreover may open up for improved reversible hydrogen absorption/desorption kinetics).

The calculated density of states (DOS) for α-NaAlH4 (at equilibrium) and β-NaAlH4 (at transition pressure) are shown in Fig. 4. Both phases have nonmetallic character with finite band gaps ($\Delta E_g$ = 5.04 and 2.35 eV for α- and β-NaAlH4, respectively). The energetic degeneration of the
predicted to transform into a volume reduction. The calculated structural parameters for the increase in the CN of the hydrogen-storage properties of the Al-hydrides suggest appreciable differences in the kinetics of the band-energy contribution to the total energy with pressure, and this may be the reason for the α-to-β phase transition.

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Al-p and H-s states together with a spatially favorable constellation of Al and H facilitate covalent bonding between Al and H. ΔE p for β-NaAlH 4 is only about half of that for α-NaAlH 4 and there are significant differences between the DOS for the two phases, especially the broadening and shifting of the bands. The partial DOS of Na shows that the s and p states are energetically degenerate in the whole energy range, while Al-s and p states are well separated in both phases.

On going from α- to β-NaAlH 4 the width of the valence band is increased from 6 to 8 eV, which is partially due to the decrease in the interatomic Al–H, Al–Na, and Na–H distances. Moreover, owing to the increase in the hybridization of Al-p with H-s at elevated pressures, the center of the Al-p band is shifted from ~1.5 eV in α-NaAlH 4 to ~3.5 eV in the β phase. The reduction in the band gap and the increase in the CN of the β phase indicate that the tendency toward metallic nature increases with pressure. Hence, one could expect appreciable differences in the kinetics of the hydrogen-storage properties of the α and β phases.

In conclusion, on application of pressure α-NaAlH 4 is predicted to transform into a β phase at 6.43 GPa with a 4% volume reduction. The calculated structural parameters for α-NaAlH 4 are in good agreement with the experimental values. Both α- and β-NaAlH 4 have nonmetallic character with finite band gaps. The coordination number of Al in β-NaAlH 4 is six as compared with four for α-NaAlH 4.

At the high pressures where β-NaAlH 4 rules, the Al-p states are more delocalized and the large DOSs at the top of the VB are moved to lower energies compared with the α phase. This leads to a gain in the band-energy contribution to the total energy with pressure, and this may be the reason for the α-to-β phase transition.

FIG. 4. Calculated DOS for (a) α- and (b) β-NaAlH 4. The Fermi level is set at zero energy and marked by the vertical lines, s electron contributions are marked with dotted regions.

Crystal structure of KAlH$_4$ from first principle calculations

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Abstract

The crystal structure of KAlH$_4$ is determined by the first principle projected augmented plane wave method taking different possible structural arrangements into consideration. From the total energy it is concluded that KAlH$_4$ crystallizes in the orthorhombic KGaH$_4$-type structure (space group Pnma) with unit-cell dimensions $a = 9.009$, $b = 5.767$, $c = 7.399$ Å. A metastable modification with $\alpha$-NaAlH$_4$-type structure is predicted in energetic close proximity to the stable phase. The electronic structure shows that KAlH$_4$ has a non-metallic character with a band gap of approximately $5.5$ eV.

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1. Introduction

Prediction and understanding of properties for various kinds of materials (even for not yet prepared phases) by theoretical means is a valuable complement to the traditional empirical methods. In many cases, money, manpower, and time can be saved by conducting theoretical simulations on a given material before testing in the laboratory. With special attention on hydrides the use of neutron diffraction and deuterated samples are normally required to obtain a correct description of the hydrogen positions in the structure; and this is particularly important when the metal matrix contains light elements. The uncertainty associated with atom co-ordinates determined for hydrogen by X-ray diffraction is large, and the thus derived metal–H distances tend to come out too short. In general compared with, say, the situation for oxides, structural understanding of hydrides [1] is very defective and fragmentary. A number of hydrides phases with $[\text{AlH}_4]^{-}$ [2–4] or $[\text{BH}_4]^{-}$ [5,6] building blocks have been synthesized in recent years and such phases have been the focus of interest for hydrogen storage and preparative organic chemistry purposes on the applied side, not to mention the theoretical aspects.

Recent experimental evidence shows that reversible hydrogen absorption/desorption proceeds smoothly in KAlH$_4$ without introduction of a catalyst [7]. KAlH$_4$ is thus different from LiAlH$_4$ and NaAlH$_4$, which have to be doped with a transition metal catalyst to obtain absorption/desorption reversibility and kinetics. Hence, KAlH$_4$ has now received considerable attention among the alkali-metal aluminum hydrides. The crystal structures of LiAlH$_4$ and NaAlH$_4$ are well known, whereas a more complete structural description for KAlH$_4$ has not yet been reported. The present structural knowledge is limited to unit-cell dimensions determined by powder X-ray diffraction (XRD) at room temperature [8]. The present theoretical study has been focused on the crystal and electronic structure of KAlH$_4$. Seven closely related potential structure types have been considered: LiAlH$_4$ (monoclinic; $P2_1/c$) [4], $\alpha$-NaAlH$_4$ (tetragonal; $I4_1/a$) [9,10], $\beta$-LiBH$_4$ (hexagonal; $P6_3mc$) [6], NaGaH$_4$ (orthorhombic; $Cmcm$) [11], NaBH$_4$ (cubic, $Fm\overline{3}m$) [12], SrMgH$_4$ (orthorhombic; $Cmc\overline{2}$) [13], and KGaH$_4$ (orthorhombic; $Pnma$) [14].

2. Computational details

To predict the ground-state structure of KAlH$_4$, we use density-functional theory (DFT) [15] within the generalized gradient approximation (GGA) [16], as implemented with a plane-wave basis in the Vienna ab initio simula-
tions package (VASP) [17]. Results are obtained using projector-augmented plane wave (PAW) [18] potentials provided with the VASP. The ions are relaxed toward equilibrium until the Hellmann–Feynman forces are less than $10^{-3}\text{eV/Å}$. Brillouin zone integration is performed with a Gaussian broadening of 0.1eV during all relaxations. All calculations are performed with 600 k points in the whole Brillouin zone and a 600eV plane-wave cutoff. In order to avoid ambiguities regarding the free-energy results we have always used the same energy cutoff and a similar k-grid density for convergence for all structural variants tested. The present type of theoretical approach has recently been successfully applied [10,19,20] to reproduce computationally ambient- and high-pressure phases.

3. Results and discussion

In order to identify the ground-state structure of KAlH$_4$, we have calculated the total energy as a function of cell volume for the seven tested possible structural variants (Fig. 1). Among them the orthorhombic KGaH$_4$-type arrangement (Fig. 2 and Table 1) is seen to have the lowest total energy with unit-cell dimensions $a = 9.009$, $b = 5.767$, $c = 7.399\text{Å}$ at 0K and ambient pressure. However, the tetragonal $\alpha$-NaAlH$_4$-type phase is energetically very close to the KGaH$_4$-type ground-state phase. This indicates that syntheses under appropriate pressure and temperature conditions may be able to generate the $\alpha$-NaAlH$_4$-type arrangement as a metastable state. The KGaH$_4$- and $\alpha$-NaAlH$_4$-type variants of KAlH$_4$ have not only a small total-energy difference, but their equilibrium volumes are similar ($V_0 = 96.15$, and $93.95\text{Å}^3$/f.u., respectively). Table 1 therefore also

![Fig. 1. Structural competition between different possible structural arrangements for KAlH$_4$.](image)

![Fig. 2. (a) The ground-state crystal structure of KAlH$_4$. (b) The slightly distorted [AlH$_4$]$^-$ tetrahedron with the interatomic Al–H distances (in Å).](image)
The theoretically obtained optimized structural parameters (Table 1) have been used to simulate the powder XRD diffractogram of KAlH₄ and this is displayed in Fig. 3 along with the observed diffractogram [7]. The generally very good agreement between the two patterns leaves no doubt that the assignment of the KGaH₄-type structure to the ground state of KAlH₄ is correct. The differences in positions and intensities of the peaks reflect the fact that the calculated pattern refers to an ideal defect-free structure at 0K, whereas the experimental diffractogram is collected at room tem-

![Fig. 3. Experimental [7] and theoretically simulated XRD patterns for KAlH₄ (Cu Kα₁ radiation; normalized with equal peak intensity for the reflection at 2θ ≈ 25°). Two peaks attributed to unreacted aluminium in the original experimental diffractogram are omitted from the comparison.](image-url)
perature on a sample burdened with defects and impurities. An ongoing experimental study [21] on KAHI4/KAlD4 has confirmed the co-ordinates of the K and Al atoms by powder XRD and work is in progress to establish the D positions by powder neutron diffraction.

KAlH4 is isostructural and isoelectronic with KGaH4, whereas other isoelectronic compounds like NaAlH4 and NaGaH4 take rather different crystal structures (see Section 1). The KAHI4 ground-state structure consists of slightly distorted [AlH4]− tetrahedra (Fig. 2b) which are separated by intermittent K+ cations (Fig. 2a). The interatomic Al–H distance (see Fig. 2b) within the [AlH4]− tetrahedra varies only by 0.9% and the bond length is as expected for an anionic complex of Al and H [22]. Each K+ cation is surrounded by 12 H atoms at distances varying between 2.717 and 3.204Å. The α-NaAlH4-type structures of the proposed metastable modification of KAHI4 also comprise tetrahedral [AlH4]− anions and K+ cations, but in a different mutual arrangement (see Fig. 1a in Ref. [10]).

The calculated cell volume vs. total energy for the KGaH4- and α-NaAlH4-type structures of KAHI4 are fit with the so-called universal equation of states [23] to derive the bulk modulus (B0) and its derivative (B′0). The thus obtained small values (Table 1) show that KAHI4, like the isoelectronic analogues LiAlH4 (B0 = 12.95 GPa [24]) and NaAlH4 (B0 = 19.30 GPa [10]), is a very soft and easily compressible material.

4. Density of states

The calculated density of state (DOS) for KAHI4 in the KGaH4-type structure is displayed in Fig. 4. From the total DOS in the lower panel it is clear that KGaH4-type KAHI4 has a non-metallic character with a band gap of ca. 5.5eV, which is close to the band gaps in other technologically interesting hydrides, viz. MgH2 (4.3eV [19]), LiAlH4 (4.8eV [24]), and NaAlH4 (5.04eV [10]). It should be recalled that theoretically derived band gaps in semiconductors and insulators may be underestimated by some 20% [25] using first principle methods.

The conspicuous feature of the total DOS is the two well separated parts in the valence band; one at −4.8 to −3.5eV and another at −1.8 to 0eV. The site-projected DOSs of K and Al show that the lower peak in the total DOS mainly originates from Al-s with small contribution from K-s, K-p, and Al-p states. It should be noted that the Al-s and Al-p states are energetically well separated in the valence band whereas the K-s and K-p states are energetically degenerated throughout the valence band. Al-p and H-s states are energetically degenerated in corresponding energy regions, which is a favourable situation for the formation of the covalent bonds within the anionic [AlH4]− complex.

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ABSTRACT: The crystal and electronic structures of the entire series of alkali aluminum and alkali gallium tetrahydrides (ABH₄; A = Li, Na, K, Rb, or Cs; B = Al or Ga) are systematically investigated using an ab initio projected augmented plane-wave method. For structural stability studies, we have considered several possible structural modifications, and reproduced successfully the equilibrium structures for the known phases LiAlH₄, NaAlH₄, KAlH₄, NaGaH₄, and KGaH₄. Moreover, we predict the equilibrium structures of the other unknown members of this series. RBaAlH₄, CsAlH₄, RBaGaH₄, and CsGaH₄ should crystallize with the KGaH₄-type structure, and LiGaH₄ should crystallize with the NaGaH₄-type structure. According to the density of states, all these compounds have nonmetallic character with a finite band gap of around 5 eV. Charge-density plot and electron localization function analyses show that the [BH₄] subunits almost look like a separate molecular species spread over the A matrix. An ionic type of interaction is present between the A and the [BH₄] units. Crystal orbital Hamilton population analyses reveal that the interaction between the B and H atoms is stronger than the other interactions present in these compounds.

Introduction

Prediction and understanding of properties of materials (comprising even not yet synthesized phases) by theoretical means is a valuable complement to the traditional empirical approach. Theoretical simulation of material properties before preparation and testing may save time, manpower, running costs, etc. Owing to the low X-ray scattering power of hydrogen, poor crystallinity, and the usual structural complexity of hydrides, these structures are often less characterized than other solids. For instance, this is the case for the (assumed technologically interesting materials) alkali aluminum and alkali gallium tetrahydrides among which only NaAlH₄, LiAlH₄, NaGaH₄, and KGaH₄ are structurally well characterized. Unit-cell volumes only are available for KAAlH₄ and LiGaH₄ and virtually no structural information exists for ABH₄ with A = Rb and Cs and B = Al and Ga. This type of compound is widely considered to be used for hydrogen storage and preparatives purposes in inorganic and organic chemistry.

A reversible process with storage of hydrogen in the form of an intermetallic hydride has several advantages over the use of conventional pressurized gas cylinders and liquid tanks. One of the major drawbacks of all metal hydrides hitherto considered for hydrogen storage in comparison to liquid hydrogen is the low mass of stored hydrogen relative to the mass of the metal hydrides. Magnesium dihydride (with 7.6 wt % stored hydrogen) represents a now prevailing optimum, but for its use as a storage material heating above 300 °C is necessary for the desorption of hydrogen. The presently most considered so-called low-and high-temperature reversible hydrides have 4–5 times lower storage capacity than MgH₂ as well as high costs.

In view of their high molar content of hydrogen, complex hydrides of light metals such as Li, Na, K, and Al have recently been in the spotlight for hydrogen storage. In 1997, NaAlH₄ was introduced as a low-weight reversible hydrogen storage material by Bogdanovic and Schwickardi. The advanced reaction mechanism for formation/decomposition of aluminohydrides is based on reversible steps, in which all constituents migrate. This is significantly different from the reaction mechanisms for conventional metal hydrides in which hydrogen atoms use interstitial crystallographic sites and are only mobile species. The thermal decomposition of AAIH₄ (A = Li, Na, or K) involves three steps:¹⁻¹⁰

\[
3\text{AAIH}_4 \rightarrow \text{A}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2
\]

(1)

\[
\text{A}_3\text{AlH}_6 \rightarrow 3\text{AH} + \text{Al} + 3/2\text{H}_2
\]

(2)

\[
3\text{AH} \rightarrow 2\text{A} + 3/2\text{H}_2
\]

(3)

In step I (at ~112, 33, and 300 °C for A = Li, Na, and K, respectively), AAIH₄ decomposes into A₃AlH₆, during which 5.3 to 2.9 wt % H is released. In step II (at ~127, 130, and 340 °C for A = Li, Na, and K, respectively), A₃AlH₆ decomposes into AH and Al, further releasing 2.6 to 1.4 wt % of H. Because of the strong bonding interaction between A and H the dry-
gen in step III is not available for practical utilization. Recent experimental evidence shows that the releasing of hydrogen from KAlH_{4} proceeds smoothly without the assistance of a catalyst. This degradation reaction is accordingly markedly different from the decomposition of NaAlH_{4} and LiAlH_{4} where homogeneous doping with a transition metal catalyst is essential for the progression of eqs 1 and 2 with good kinetics. To get more insight into the properties of these systems, improved structural information is needed, and the present study is aimed at the crystal and electronic structures of ABH_{4}, A = Li, Na, K, Rb, or Cs; B = Al or Ca at ambient pressure.

Computational Details

To predict the ground-state crystal and electronic structures, we have used density-functional theory (DFT) within the generalized-gradient approximation (GGA),\textsuperscript{15} as implemented with a plane-wave basis in the Vienna ab initio simulations package (VASP).\textsuperscript{16} Results are obtained using projected-augmented wave (PAW) potential provided with VASP. The PAW potentials explicitly treat one valence electron for H (1s\textsuperscript{1}), Li (2s\textsuperscript{1}), and Na (3s\textsuperscript{1}) seven for K (4s\textsuperscript{1}, 4p\textsuperscript{1}) and Rb (4p\textsuperscript{1}, 5s\textsuperscript{1}), nine for Cs (5s\textsuperscript{1}, 5p\textsuperscript{1}, 6s\textsuperscript{1}), and three for Al (3s\textsuperscript{1}, 3p\textsuperscript{1}) and Ga (4s\textsuperscript{1}, 4p\textsuperscript{1}). The ions are steadily relaxed toward equilibrium until the Hellmann–Feynman forces are less than 10\textsuperscript{3} eV/Å during all relaxations. Experimentally established structural data were used as input for the calculations when available. For the tetragonal NaAlH_{4} structure we used 432 k points in the whole Brillouin zone. A similar density of k points was used for the other structures. To avoid ambiguities regarding the free-energy results, we have used the same energy cut-off and similar k-grid densities in all calculations. At least 0.01 meV/Å was used as a criterion on the self-consistent convergence of the total energy, and the calculations reported here used a plane wave cut-off of 500 eV. A similar approach was successfully applied for the case of MgH_{2}, where the three experimentally observed high-pressure phases were reproduced successfully and two additional high-pressure phases were predicted.\textsuperscript{16} To identify the bond strength, we have used the crystal orbital Hamiltonian population (COHP)\textsuperscript{17} analysis, which is implemented in the TBLMTO-4\textsuperscript{17} package.\textsuperscript{18} A measure of the magnitude of bonding was obtained by computing COHP, which is the Hamilton population weighted density of states, similar to the well-known crystal-orbital-overlap population. In a simplified picture, negative COHP indicates a bonding character and positive, antibonding character. The bulk moduli have been obtained using the so-called universal equation-of-state fit for total energy as a function of the volume.

Results and Discussion

For our simulations, we have chosen seven different possible closely related structure types, they are a-LiAlH\textsubscript{4} (monoclinic; P2\textsubscript{1}/c),\textsuperscript{10} a- NaAlH\textsubscript{4} (tetragonal; P4\textsubscript{1}2\textsubscript{1}2\textsubscript{1}),\textsuperscript{10} b-LiBH\textsubscript{4} (hexagonal; P6\textsubscript{3}mc),\textsuperscript{21} a-NaGaH\textsubscript{4} (orthorhombic; Cnmn),\textsuperscript{22} NaBH\textsubscript{4} (cubic, F43m),\textsuperscript{23} SrMgH\textsubscript{4} (orthorhombic; Cmcm),\textsuperscript{24} NaAlH\textsubscript{4} (orthorhombic; Cmcm),\textsuperscript{25} and a-RgAlH\textsubscript{4} (orthorhombic; Pnma).\textsuperscript{26} In our previous communications on LiAlH\textsubscript{4},\textsuperscript{26} NaAlH\textsubscript{4},\textsuperscript{27} and KAlH\textsubscript{4},\textsuperscript{28} we have reported on successful reproduction of the ground-state structures and prediction of new high-pressure modifications of LiAlH\textsubscript{4} and NaAlH\textsubscript{4}. In this work, we present the ground-state structures for the remaining seven compounds in the ABH\textsubscript{4} series. We have also identified potential high-pressure phases for some of these compounds, but these aspects will be accounted for in a forthcoming paper. To identify the equilibrium structure of the ABH\textsubscript{4} phases, we have adopted the following procedure. First, for each trial structure, we have optimized the atomic coordinates and cell parameters globally using stress and force minimization, and thus identified the optimized cell volume, atomic coordinates, and unit-cell dimensions. In the following step, we varied the unit-cell volume between \sim \sim 28 and +15% in steps of 5% and relaxed all atom coordinates and unit-cell dimensions globally for each volume. The resulting cell volume vs free-energy relations for the considered possible structural arrangements for RgAlH\textsubscript{4} are illustrated in Figure 2. The equilibrium volumes and bulk moduli were extracted from the calculated energy vs cell volume data by fitting them to the "universal equation of state"
Figure 2. Calculated cell volume vs free energy curves for KGaH$_4$ in different possible arrangements (indicated on the illustration).

Figure 3. Variation in the cell volume along the ABH$_4$ series.

Proposed by Vinet et al.\textsuperscript{32} (virtually the same results were obtained by fitting to the Birch\textsuperscript{33} or Murnaghan\textsuperscript{34} equation).

From the total-energy minimization procedure, we have extracted the equilibrium structure parameters. In good agreement with the experimental findings for KGaH$_4$, the orthorhombic prototype structure takes the lowest energy (see Figure 2) with cell parameters in good agreement with the experimental\textsuperscript{35} findings (see Table 1). In addition to the experimentally known prototype structure, a variant with α-LiAlH$_4$-type structure also exists close in energy (estimated energy difference only 0.02 eV/f.u.). Both structures have almost similar equilibrium volume (96.62 and 96.43 Å$^3$/f.u. for the KGaH$_4$ and α-LiAlH$_4$ type, respectively). This indicates that syntheses under appropriate pressure and temperature conditions may be able to generate the α-LiAlH$_4$-type arrangement as a metastable state. Similarly, for the other known compounds in the series, experimentally identified structures (α-LiAlH$_4$, NaAlH$_4$, and NaGaH$_4$) proved to have the lowest energy among the considered alternatives. The good agreement (1–2% in unit-cell dimensions) between experimental and calculated structure data (Table 1) demonstrates the reliability of the calculation and lends confidence to the structural data extracted for the hitherto unknown members of the series (remembering that our calculations refer to 0 K, viz. temperature effects are not taken into account). From the total-energy minimization procedure, we have found that KAlH$_4$, RbAlH$_4$, CsAlH$_4$, RbGaH$_4$, and CsGaH$_4$ stabilize in the KGaH$_4$-type structure (see Table 1), and the following discussion is valid only for these isostructural phases. In the KGaH$_4$-type structure, the B atoms are tetrahedrally coordinated to four hydrogen atoms that are in three crystallographically different positions. The [BH$_4$]$^-$ (anion) tetrahedra (which are slightly distorted) are kept apart by the A (here A = K, Rb, Cs) cations. The average A–H separations within the [BH$_4$]$^-$ tetrahedra vary from 1.602 (RbGaH$_4$) to 1.616 Å (KAlH$_4$) (two A–H distances of one kind and two others of a different kind). Each A$^+$ is surrounded by 12 H atoms, with A–H distances varying between 2.689 (KAlH$_4$) and 3.092 Å (CsAlH$_4$). Among the 10 considered phases KAlH$_4$, RbAlH$_4$, CsAlH$_4$, KGaH$_4$, RbGaH$_4$, and CsGaH$_4$ are isostructural, whereas LiAlH$_4$, NaAlH$_4$, and NaGaH$_4$ take different structural arrangements. On going from A = Li to Cs in the Ga-based compounds, the calculated equilibrium volumes vary almost linearly (Figure 3). This concurs with the fact that on moving downward on the periodic table the atomic radii increases roughly linearly, a behavior reflected in the cell volumes. On the other hand, among the Al-based compounds, the cell volume of NaAlH$_4$ deviates from a linear pattern in that LiAlH$_4$ and NaAlH$_4$ have almost similar equilibrium volume (276.41 and 276.88 Å$^3$, respectively).

The preference for different packing among the ABH$_4$ series can readily be rationalized by their Ionic radii (0.99, 0.97, 1.37, 1.52, and 1.67 Å for Li, Na, K, Rb, and Cs, respectively). A common feature for the series is the comparatively large [BH$_4$]$^-$ building block and its size determining influence of the overall structure. The interatomic A–H distance within the [BH$_4$]$^-$ unit is almost the same (running between 1.60 and 1.64 Å; shortest in the AGaH$_4$ series largest for KAlH$_4$). On moving from Li to Cs in these series, the calculated A–H distance varies linearly and the H–H separation increases from 2.56 to 2.71 Å. In LiAIH$_4$, the large [AIH$_4$]$^-$ anion tends to adopt hexagonal close packing, which would minimize the hole size for the small Li$^+$ cation (the monoclinic β angle is ~112°, viz. close to the hexagonal β = 120°).
Table 1. Optimized Structural Parameters, Bulk Module ($B_0$), and its Pressure Derivative ($B'_0$) for ABH₄ Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>unit-cell dimensions (Å)</th>
<th>atomic positions</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-LaNH₄ (prototypic: P2₁/c)</td>
<td>a = 4.8354 (4.8174)* b = 7.8259 (7.8003)* c = 7.8419 (7.8214)* β = 111.978 (112.259)*</td>
<td>Li(4a): 0.5999, 0.4652, 0.6345 (0.5663, 0.4656, 0.6265)* Al(4c): 0.1331, 0.2017, 0.9319 (0.1036, 0.2033, 0.9302)*</td>
<td>12.95</td>
<td>4.10</td>
</tr>
<tr>
<td>α-NaAlH₄ ( proto-type: I₄/m)</td>
<td>a = 4.9965 (4.9801)* b = 11.0928 (11.1483)*</td>
<td>Na(4e): 0, 0.14, 0.68</td>
<td>19.31</td>
<td>4.77</td>
</tr>
<tr>
<td>K₄H (KGaH₆-type: Pnma)</td>
<td>a = 8.950 (8.814)* b = 5.863 (5.819)* c = 7.894 (7.501)*</td>
<td>K(4c): 0.1778, 0.14, 0.162</td>
<td>10.34</td>
<td>4.61</td>
</tr>
<tr>
<td>Rb₂H (KGaH₆-type: Pnma)</td>
<td>a = 5.956</td>
<td>Rb(4c): 0.1823, 0.14, 0.159</td>
<td>9.22</td>
<td>4.94</td>
</tr>
<tr>
<td>Ca₃H (KGaH₆-type: Pnma)</td>
<td>a = 10.520 b = 0.0945 c = 0.0232</td>
<td>Ca(4e): 0.1868, 0.14, 0.160</td>
<td>8.35</td>
<td>5.42</td>
</tr>
<tr>
<td>Li₂GaH₄ (NafAs-type: Cmcm)</td>
<td>a = 6.5275</td>
<td>Li(4c): 0, 0.4390, 1/4</td>
<td>11.97</td>
<td>5.04</td>
</tr>
<tr>
<td>Na₃GaH₄ (proto-type: Cmcm)</td>
<td>a = 7.1102 (7.07)* b = 6.4717 (6.60)* c = 7.1069 (7.06)*</td>
<td>Na(4a): 0.3439, 1/4 (0.3370, 1/4)*</td>
<td>13.19</td>
<td>4.93</td>
</tr>
<tr>
<td>KGaH₄ ( proto-type: Pnma)</td>
<td>a = 9.1338 (9.87)* b = 5.6467 (5.61)* c = 7.3990 (7.30)*</td>
<td>K(4c): 0.1866, 0.14, 0.1616 (0.1866, 1/4, 1.1537)</td>
<td>10.15</td>
<td>4.95</td>
</tr>
<tr>
<td>Rb₂GaH₄ (KGaH₆-type: Pnma)</td>
<td>a = 9.5390</td>
<td>Rb(4c): 0.1781, 0.14, 0.169</td>
<td>9.41</td>
<td>5.06</td>
</tr>
<tr>
<td>Ce₃GaH₄ (KGaH₆-type: Pnma)</td>
<td>a = 10.0154 b = 0.0905 c = 0.0751</td>
<td>Ce(4e): 0.1794, 0.14, 0.163</td>
<td>8.22</td>
<td>5.20</td>
</tr>
</tbody>
</table>

* From ref 18. † From ref 29. ‡ From ref 30. § From ref 31. ¶ From ref 25.

Experimental values for bulk modulus are not available for all of these compounds, and hence theoretical predictions of $B_0$ are of interest. A relationship between binding energy and interatomic distances has been discovered for so-called bimetallic adhesion, 35 chemisorption on metals, 25 and metallic cohesion. 27 Vinet et al. 25 proposed a universal equation of state (UES) for all classes of solids in compression, which is claimed to be superior to that of the Birch–Murnaghan EOS. 36 The calculated bulk modulus varies almost linearly along the series (Table 1; except for NaAlH₄) viz. consistent with the volume variation in this series. The maximum values of $B_0$ for NaAlH₄ suggest that enhanced bond strength for this compound may be the cause of the drop in the cell volume relations. The magnitude of $B_0$ classifies these ABH₄ compounds as easily compressible materials (the $B_0$ values in Table 1 being about 3 times smaller than for MgH₂).

Density of States (DOS). The total DOS for ABH₄ shows close similarities (data for the AGaH₄ series being reported in Figure 4). The partial density of states (PDOS) is a useful tool to analyze the nature of the chemical bonding in solids; 25 hence we display PDOS curves for KGaH₄ in Figure 5. In general, these ABH₄ compounds have a finite energy gap between the valence and conduction bands, and accordingly they exhibit nonmetallic features. The total DOS (Figure 4) for the AGaH₄ phases comprises three well-separated regions; region I: below ~6 eV, region II: from ~3 to 0 eV, and region III: above 5 eV (occupied states). On going from LiGaH₄ to CsGaH₄, the width of the bands (in particular the VB; see Figure 5) is narrowed. Recalling that the Ga–H distance does not vary much along the AGaH₄ series it seems safe to conclude that it is the enhancement in the A–H interaction which is the main reason for the reduction in the VB width.

From an electronic point of view, the bonding B–H interaction should be of a covalent nature, whereas the A–H interaction should be ionic. Looking at the site projected DOS of K and Ga (middle panels of Figure 5),
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Figure 4. Calculated total density of states for AGaH$_4$ compounds. The Fermi level is set at zero energy and marked by vertical lines.

Figure 5. Calculated partial density of states for KGaH$_4$. The Fermi level is set at zero energy and marked by vertical dotted lines; s-electron contributions are depicted in gray.

the region I is mainly originating from Ga-s states with only small contribution from K-s and -p states. Region II is mainly contributed by Ga-p, K-s and -p, and H-s states. Ga-s and -p states are energetically well separated in the VB region, whereas K-s and -p states are energetically degenerate. The degeneration of Ga-p and H-s states in the VB region reflects the elementary text book picture of sp$^3$ hybridization in a tetrahedral unit like [GaH$_4$] (with a spatially favorable situation for such hybridized bonding). The calculated band gap ($E_g$) for these compounds varies from 4.5 to 5.5 eV, LiGaH$_4$ having the smallest and KAIH$_4$ the largest band gap. RbAIH$_4$, KGaH$_4$, RbGaH$_4$, and CsGaH$_4$ have $E_g \approx 5$ eV, which may reflect the isostructural character of these phases. The calculated $E_g$ values are quite close to that of other technologically important hydrides$^{18}$ like MgH$_2$ (4.3 eV). It should be recalled that theoretically derived band gaps in semiconductors and insulators may be underestimated by 20–50 using first-principle methods.$^{29}$

Charge Density and Electron Localization Function. To get better insight into the chemical bonding in these compounds, we have made charge-density distribution and electron localization function (ELF) analyses. From an application point of view, such analyses may help to identify potential substitution elements that can improve the properties of such materials. Like DOS, the charge-density distribution and ELF show similar features for series such as this, and the following account will therefore be focused on KGaH$_4$.

Figure 6 shows the calculated valence charge density (obtained directly from the self-consistent calculations) within the (101) plane. At the K, Ga, and H sites it is clear that the highest charge density resides in the immediate vicinity of the nuclei. The predominant covalent nature of the bonding between Ga and H is further confirmed by the finite charge between these atoms. The H-s electrons are tightly bound to the Ga-p states, and the formation of sp$^3$ hybridization concurs with [GaH$_4$] units in a K matrix (in support of the conclusions form DOS). The electron distribution between K and the [GaH$_4$] unit is almost zero (charge depleted; see Figure 6), viz. an ionic type of interaction is present between [GaH$_4$] and K.

ELF is a ground-state property that discriminates in a quantitative way between different kinds of bonding.$^{48,49,67}$ In the implementation for density-functional theory, this quantity depends on the excess of local kinetic energy due to the Pauli principle. In general, ELF becomes 1 either for single-electron or any two-electron singlet-wave function. In a many-electron system ELF becomes close to 1 in regions where electrons are paired to form a covalent bond, and also close to 1 for a region with an unpaired lone electron of a dangling bond. In a homogeneous electron gas ELF equals 0.5 at any electron density, values of this order indicating regions with bonding of a metallic character. The ELF value at Ga and H in KGaH$_4$ is 1, again consistent with covalent type of interaction between the Ga and H. Figure 7, right panel shows an ELF plot at an iso-surface value of 0.75, which further emphasizes the distribution of distinct [GaH$_4$] units in a K matrix. The ELF value at the K site is $\sim 0.2$ and between the K site and the interstitial region ELF is virtually zero. The ELF findings thus reinforce the ionic bonding between K$^+$ and [GaH$_4$]$^-$ with strong covalent internal bonding within the latter units.

Crystal Orbital Hamilton Population Analysis. To evaluate the bond strength between the involved atoms, we have performed COHP analysis. Integrated COHP (ICOHP) up to $E_F$ gives the magnitude of the bond strength and the result from such COHP analyses for KGaH$_4$ is shown in Figure 8 for all possible combinations of the involved constituents. The VB comprises mainly bonding orbitals (negative COHP), whereas antibonding orbitals are found some $\sim 3.5$ eV above $E_F$. The most notable feature in Figure 8 is the remarkable
strength of the Ga–H interaction (≈2.62 to 3.44 eV in ICOHP, similar for all B–H interactions in this series) compared to the other interactions. Moving from A = Li to Cs the B–H interaction (covalent bond strength) is reduced (both in the Al and Ga series). According to the calculated ICOHP for these compounds, the Al–H bond is stronger than the Ga–H bond. This indicates that the stability (and hence the decomposition temperature) in the Al series is higher than in the Ga series. It implies that the partial substitution of Li by other alkaline elements in materials such as Li₁₋ₓNaₓAlH₄, Li₁₋ₓKₓAlH₄ or Li₁₋ₓKₓAlₓ⁻₋ₓGaₓH₄ may give lower decomposition temperatures.

In addition to the B–H interaction, the A–H (≈0.31 to 0.43 eV) and A–B (≈0.09 to 0.12 eV) interactions also have considerable ICOHP values in these ABH₄ compounds, however, appreciably smaller than the B–H interactions. The ICOHP for H₁–H₂ up to E₅ has an almost negligible value, which perhaps indicates the presence of both bonding and antibonding states in this interaction. Thus with both bonding and antibonding states present in almost equal amounts in the VB region the covalent interaction between the hydrogen atoms will not contribute significantly to the stability of these systems. It implies that the B–H interaction is the main cause for the relatively high decomposition temperature of these phases.

**Conclusion**

The crystal structure of an entire series of ABH₄ compounds have been investigated from first-principle density-functional calculations for different possible structural modifications. The calculated atomic position and cell parameters are in very good agreement with experimental findings for LiAlH₄, NaAlH₄, KAlH₄, Na-GaH₄, and KGaH₄. The crystal structure for RhAlH₄, CsAlH₄, LiGaH₄, RbGaH₄ and CsGaH₄ are predicted. The values of calculated bulk modulus indicate that all these materials should be easily compressible. A density of state examination shows that these compounds have a nonmetallic nature and with calculated band gaps around 5 eV. The calculated Al–H and Ga–H distances are almost the same for all compounds, implying that all of these compounds have almost the same size of the [BH₄]⁻ structural units. From the partial DOS, charge density, and ELF study, it is concluded that these compounds are ionic materials with covalent interaction between B and H in the [BH₄]⁻ units and ionic between the [BH₄]⁻ and A⁺. From the COHP analysis, we have identified that the magnitude of the B–H interaction is stronger than the other interactions in these compounds. The Al(Ga)–F bond strength is reduced when we move from the top to the bottom of the alkaline metals in the periodic table. This suggests that substitution of...
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Figure 8. COHP curves for KGaH₄ referring to the combinations Ga-H₁, K-H₁, H₁-H₂, and K-Ga.

Li by an other alkali elements in LiAlH₄ may reduce the decomposition temperature.

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Structural stability of alkali boron tetrahydrides ABH₄ (A = Li, Na, K, Rb, Cs) from first principle calculation

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Abstract

The ground-state crystal structures of the boron hydride series ABH₄ (A = Li, Na, K, Rb, Cs) have been established from first principle projected-augmented plane-wave calculations by considering different possible structural arrangements and subjecting the test structures to structural relaxations. LiBH₄ crystallizes with orthorhombic symmetry (KGaH₄-type; P̅nma), NaBH₄, KBH₄, and RbBH₄ with tetragonal symmetry (γ-NaBH₄-type; P̅4/nmc), and CsBH₄ in another tetragonal space group (β-NaBH₄-type; P̅4_2_1/c). A possible reason for the transitions from lower- to higher-symmetric structures along the series has been advanced. The theoretically derived positional parameters for LiBH₄ gives an almost ideal tetrahedral configuration for the [BH₄⁻] complex whereas the experimental results show that these units are strongly distorted. The theoretically derived structures for KBH₄, RbBH₄, and CsBH₄ differ appreciably from the experimentally established low-temperature structures. From total-energy calculations it seems that syntheses under appropriate pressure and temperature conditions may be able to generate a number of metastable phases of the ABH₄ series. The density-of-states characteristics reveal that all these ABH₄ compounds exhibit insulating behavior with band gaps varying between 5.5 and 7.0 eV.

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Keywords: Electronic structure; Crystal structure; Structural stability; Alkali boron tetrahydrides

1. Introduction

Hydrogen is considered as an ideal energy carrier. However, hydrogen storage with a safe, effective, and cheap storage system is crucial for, e.g. hydrogen-based fuel cells or hydrogen-driven combustion engines. Metal hydrides can typically absorb 1–2 hydrogen atoms per metal atom and have large storage capacities by volume (up to 150 kg H₂ m⁻³ for, e.g. Mg₂FeH₆). However, due to the large atomic mass of the metals concerned, the storage capacity by weight is limited to less than 2.5 wt. % [1, 2]. The light elements of groups I–III, e.g. Li, Be, Na, Mg, B, and Al, form a large variety of complex hydrides which are interesting from a storage point of view because of their light weight (the number of hydrogen atoms per matrix atom being in many cases around 2). Alkali boron tetrahydrides (with a maximum storage capacity of up to 18.2 wt. % in LiBH₄) and alkali aluminum tetrahydrides (with a maximum storage capacity of up to 10.6 wt. % in LiAlH₄) are interesting hydrogen storage materials, but they are unfortunately very stable and are dehydrogenated only at elevated temperatures. Recent experimental evidences show that LiAlH₄ and NaAlH₄ after mechano-chemical processing under ambient conditions in the presence of certain transition-metal catalysts [3–6] rapidly release 7.9 and 5.6 wt. % of H, respectively. Although it is now accepted that these materials will never meet the FreedomCar goals (where 5 wt. % stored hydrogen and operating temperature below 100 °C are the targets), they exhibit about 3 wt. % reversible hydrogen storage capacity with desorption below 100 °C when doped with Ti and/or other additives. Perhaps modified complex hydrides are the only presently known materials that have the potential to meet the FreedomCar goals [7]. Recent experimental evidence shows that the hydrogen desorption from LiBH₄ is efficiently catalyzed by SiO₂ to an amount of 13.5 wt. % and onset hydrogen liberation at 200 °C [8]. These findings promptly released a...
2. Computational details

To predict the ground-state crystal and electronic structures in the ABH₄ series, we have used density-functional theory (DFT) [9] within the generalized-gradient approximation (GGA) [10] as implemented with a plane-wave basis in the Vienna ab initio simulations package (VASP) [11]. Calculations were performed using projected-augmented wave (PAW) [12] potentials provided with the VASP. The PAW potentials explicitly treat one valence electron configurations for H (1s), Li (2s²), and Na (3s⁵); seven for K (3p⁶, 4s¹) and Rb (4p⁶, 5s¹); nine for Cs (5s⁵, 5p⁵, 6s¹); and three for B (2s², 2p²). The atoms are steadily relaxed toward equilibrium until the Hellmann–Feynman forces have become less than 10⁻³ eV/Å during all relaxations. Experimentally established structural data were used as input for the calculations when available. For the orthorhombic α-LiBH₄ structure we used 360 k points in the whole Brillouin zone. A similar density of k points were used for the other structures. In order to avoid ambiguities regarding the free-energy results we have used the same energy cutoff and similar k-grid densities in all calculations. At least 0.01 meV/atom was placed as a criterion on the self-consistent convergence of the total energy, and the calculations reported here used a plane-wave cutoff of 500 eV. A similar approach has been successfully applied for several complex hydrides, and a more detailed description of the computational procedure is given in Refs. [13–16].

3. Results and discussion

For the theoretical simulation we have chosen 10 different possible, closely related structure types, viz. LiAlH₄ (monoclinic; P2₁/c) [17], Na-AlH₄ (tetragonal; I₄/1/a) [14,18], β-LiBH₄ (hexagonal; P6₃mc) [19], NaGaH₄ (orthorhombic; Cmcm) [20], BaSO₄ (cubic; Fm3m), α-NaBH₄ (cubic; Fm3m) [21], SmMgH₄ (orthorhombic; Cc2/c) [22], β-KBH₄ (tetragonal; P4₁/nmc), γ-NaBH₄ (tetragonal; P4₂/nmc), and KGaH₄ (orthorhombic; Pnma) [23]. For the calculations according to the α-NaBH₄-type structure hydrogen is placed in position 32f with 50% occupancy [24] and particular care was taken when simulations were made according to this structural description. The procedure involved systematic distribution of the hydrogens in different constellations, and for each of these arrangements derivation of the total energy was carried out. The configuration which gave the lowest value for the total energy was declared as the hydrogen arrangement for α-NaBH₄-type variants. Effects of zero-point motion were not considered, since estimation of these requires access to phonon modes which cannot be calculated within the present scope. However, the now prevailing experience suggests that the neglect of zero-point-motion effects does not invalidate the present conclusions on phase stability.

3.1. Structural relations

At ambient conditions LiBH₄ (α-LiBH₄) crystallizes with an orthorhombic (KGaH₄-type) structure in which each [BH₄]⁻ anion is surrounded by four lithium Li⁺ and each Li⁺ by four [BH₄]⁻, both in tetrahedral configurations (Fig. 1a–1c, Table 1). At ca. 381 K α-LiBH₄ undergoes a structural transition to β-LiBH₄, but conflicting results have been reported concerning the symmetry of the phase formed. First β-LiBH₄ was believed [26,27] to belong to the tetragonal class, but the recent experimental study of Soulá et al. [19] shows that the symmetry is hexagonal (see Table 1). As seen from Fig. 1g the structural arrangements of α- and β-LiBH₄ are closely related.

All other members of the ABH₄ series (A = Na, K, Rb, Cs) crystallize with a cubic NaCl-like structural arrangement at room temperature in which [BH₄]⁻ are octahedrally surrounded by A⁺ [28,29]. At low temperature the α modifications of the ABH₄ compounds show various behaviors [24,25,30]. α-NaBH₄ and α-KBH₄ transform into closely related tetragonal arrangements (space group P4/2/nmc for β-NaBH₄ and P4/2/nmc for β-KBH₄; see Table 1 and Fig. 1c–e,h,i and Refs. [24,25] for further details). Note that (within the framework of the two different space groups) β-NaBH₄ and β-KBH₄ obtain identical atomic coordinates for Na, K, and B whereas the positional parameters for the H atoms differ (c/a is also almost the same for the two phases). The low-temperature β and room-temperature α modifications of NaBH₄ and KBH₄ have also markedly similar structural arrangements (see Fig. 1c–e,h,i), and the main variables causing structural distinctions are the lattice parameters.

In the case of LiBH₄, NaBH₄, and KBH₄ the low-temperature transitions lead to more ordered structural arrangements in which the hydrogen atoms surround boron in tetrahedral configuration. RbBH₄ and CsBH₄ appear not to exhibit phase transitions below room temperature, viz. their cubic structures are maintained [24]. However, specific heat measurements [30] suggest that there are (anisotropic) anomalies at 44 and 27 K in RbBH₄ and CsBH₄, respectively. Similarly Renaudin et al. [24] suggest on the basis of low-temperature powder neutron diffraction (PND) findings that it should be possible to form superstructures of RbBH₄ and CsBH₄, but the resolution in the diffraction data prevented a firm conclusion. From this point of view a theoretical examination of the latter materials is highly desirable.

In order to identify low-temperature phases of the ABH₄ series we have calculated (see Refs. [14–16]) for details about...
Fig. 1. Upper row: crystal structure of (a) $\beta$-LiBH$_4$ (KGaH$_4$ type; Pnma), (b) $\beta$-LiBH$_4$ (prototype; P6$_3$mc), (c) $\beta$-KBH$_4$ (prototype; P$\bar{2}$1$_1$), (d) $\gamma$-NaBH$_4$ (prototype; P4$_1$2$_1$2$_1$mc), and (e) $\alpha$-NaBH$_4$ (prototype; Fm\overline{3}m). Lower row: two-dimensional representation of (f) the $\alpha$-NaBH$_4$ matrix. Projection of schematic structural relationship between (g) $\alpha$- and $\beta$-LiBH$_4$, (h) $\alpha$- and $\beta$-NaBH$_4$, and (i) $\alpha$- and $\gamma$-NaBH$_4$. 
the computational procedure) the total energy as a function of cell volume for the ten above mentioned possible structural variants. Among the 10 tested variants for LiBH₄ the orthorhombic KGaH₄-type arrangement (Fig. 1a, Table 1) is found to have the lowest total energy (Fig. 2) with unit-cell dimensions \(a = 7.3635\,\text{Å}, \ b = 4.3982\,\text{Å}, \) and \(c = 6.8032\,\text{Å}\) at 0 K and ambient pressure, which agree with recent experimental findings [19] within 3% (2.5, ~0.9, and ~3% for \(a, \ b, \) and \(c, \) respectively). The calculated positional parameters for \(\alpha\text{-LiBH}_4\) gives a nearly ideal tetrahedral \([\text{BH}_4]^-\) complex (with H–B–H bond angles ranging between 108° and 112°) whereas the experimental results [19] suggest that the complex is highly distorted (bond angles: 85°–120° [19]). The theoretically derived B–H distances in \(\alpha\text{-LiBH}_4\) turned out to be almost equal (ca. 1.22 Å), whereas experimental studies gave different results (1.28–1.44 Å [8], 1.01–1.28 Å [19]). Assuming that the thus exposed mutual discrepancy is real it seems likely that the structural arrangements of LiBH₄ as a whole or in parts are sensitive to temperature. The theoretical results are valid for 0 K and absence of external pressure or other perturbations. Hence, a largely ideal tetrahedral \([\text{BH}_4]^-\) configuration is quite conceivable under these conditions. The experimental findings refer to room temperature and in the experimental reality the KGaH₄-type atomic arrangement represents the room-temperature situation whereas the \(\beta\text{-LiBH}_4\) occurs as a high-temperature modification, viz. opposite to the order implied by Fig. 2. However, the involved energy difference between the \(\alpha\) and \(\beta\) forms according to Fig. 2 is only 0.2 eV/f.u., which means that the competition between the two types of structural arrangements will be sensitive to synthesis and examination temperature. In the theoretical situation also the \(\beta\text{-NaBH}_4\) and \(\beta\text{-KBH}_4\) type atomic arrangements enter into the picture together with the \(\alpha\) and \(\beta\) forms of LiBH₄ all within the 0.2 eV/f.u. energy range (see Fig. 2). This indicates that syntheses under appropriate pressure and temperature conditions may stabilize LiBH₄ in either of the \(\beta\text{-NaBH}_4\) or \(\beta\text{-KBH}_4\) types or mixtures thereof as metastable phases. Fig. 2 clearly brings out that on application of pressure \(\alpha\text{-LiBH}_4\) should transform to a \(\beta\text{-KBH}_4\) type atomic arrangement. We have in fact, established several such pressure-induced phase transitions in the ABH₄ system (\(A = \text{Li, Na, K, Rh, Cs}; B = \text{B, Al, Ga}\) and a full account of the findings will be reported in a forthcoming publication (see also Refs. [14,16]).

The theoretical calculations predict that at lower temperatures NaBH₄ crystallizes in the tetragonal \(\beta\text{-NaBH}_4\) (prototype) structure, which is consistent with the experimental results. The calculated unit-cell dimensions and positional parameters (Table 1) are in good agreement with the experimental findings [25]. Similarly, the calculations show that KBH₄ and RbBH₄ also stabilize in the \(\beta\text{-NaBH}_4\) type structure whereas CsBH₄ takes the \(\beta\text{-KBH}_4\) type structure. However, the experimentally identified structures \(\beta\text{-KBH}_4\) (prototype) for KBH₄ at 1.5 K [24] and \(\alpha\text{-NaBH}_4\) type for RbBH₄ and CsBH₄ [24]) are quite different from those theoretically predicted. Recalling that the structural arrangements of the

![Fig. 2. Calculated cell volume vs. total energy curves for LiBH₄ in different possible arrangements (structure types indicated on the illustration). A predicted pressure induced transition to \(\beta\text{-KBH}_4\) type structure is marked by the arrow.](image1)

![Fig. 3. Calculated ground-state total DOSs for the ABH₄ series. Fermi level is set at zero energy and marked by the vertical dotted line; occupied states are shaded.](image2)
Comparing the equilibrium structures along the series (from LiBH₄ to CsBH₄), it is seen that the structural arrangement is systematically changed from lower to higher symmetry. Increasing temperature plays the same role as increasing cation size in this respect. For example, at low temperatures KBH₄ stabilizes in a tetragonal structure which transforms to a higher-symmetric cubic structure at higher temperatures. This reflects the fact that the increasing thermal movements of the atoms on increasing temperature perturb the chemical bonds to become more isotropic. Similarly, the smaller cations give rise to more impurity between the size of A⁺ and [BH₄]⁻ and hence a less isotropic bonding situation. Moreover, the smaller A⁺ cations are more electronegative than the larger ones and the increased covalent contribution to the bonding gives rise to a more directional bonding character.

Table 1

Optimized unit-cell dimensions (in Å), atom coordinates, bulk modulus (Bₑ in GPa), and the derivative of bulk modulus (Bₑ) for ABH₄ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit-cell dimensions</th>
<th>Atom coordinates</th>
<th>Bₑ</th>
<th>Bₑ'</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-LiBH₄ (KCa₂H₂ type; Pnma)</td>
<td>a = 7.3635 (7.1786) b = 4.3982 (4.4369) c = 6.5965 (6.8032)</td>
<td>Li (4c): 0.1549, 1/4, 0.1142 (0.1568, 1/4, 0.1015) B (4c): 0.3141, 1/4, 0.4244 (0.3040, 1/4, 0.4305)</td>
<td>15.3</td>
<td>3.9</td>
</tr>
<tr>
<td>β-LiBH₄ (prototype; P6₃mcm)</td>
<td>a = 4.1956 (4.2763)</td>
<td>Li (2b): 1/3, 2/3, 0.96645 (1/3, 2/3, 1)</td>
<td>20.8</td>
<td>4.4</td>
</tr>
<tr>
<td>δ-LiBH₄ (prototype; Fd3m)</td>
<td>a = 6.6013 (6.9484)</td>
<td>Cs (2d): 0.2157, 0.0272, 0.4249 (0.1720, 0.054, 0.4280)</td>
<td>27.4</td>
<td>5.7</td>
</tr>
</tbody>
</table>

* Experimental values from Ref. [19].
* Experimental values from Ref. [20].
* H statistically occupy only 50% of the 32f site [24].
* Metastable phase.

arrangements will be very small. For example, for KBH₄ the estimated equilibrium volume for atomic arrangements according to the β-NaBH₄, β-KBH₄, and α-NaBH₄ type is 76.05, 76.34 and 76.81 Å³/f.u., respectively, and the energy difference for the two latter modifications with respect to the former is only 5.6 and 23 meV, respectively. This indicates that also these compounds will be sensitive to temperature and/or pressure conditions used during their syntheses. For this reason, Table 1 gives structural information of potential metastable modifications of the ABH₄ series in addition to the equilibrium structures. In general, the calculated structural data are in good agreement with the experimental findings whenever data are available for comparison (Table 1; less than 2.2% in unit-cell dimensions which is well within the limit of the state-of-the-art accuracy for DFT calculation).
Experimental data for the bulk modulus ($B_0$) are not available for the ABH$_4$ compounds and hence the theoretically predicted of $B_0$ values in Table 1 should be of interest. An almost linear variation of $B_0$ with the size of A$^+$ occurs along the series, except for NaBH$_4$ which show a maximum value for $B_0$ and suggests an enhanced bond strength for this compound. It is interesting to note that on comparison of $B_0$ for the AAlH$_4$ and AGaH$_4$ series with the ABH$_4$ series, the latter exhibits higher $B_0$ values than the two former series, implying that the ABH$_4$ series are relatively harder materials than those of the AAlH$_4$ and AGaH$_4$ series. However, the magnitude of $B_0$ classifies also the ABH$_4$ compounds as easily compressible materials ($B_0$ being about 2–3 times smaller than $B_0$ for MgH$_2$). The soft character of the ABH$_4$ materials arises from the ionic bonding between A$^+$ and the [BH$_4$]$^-$ complexes. Although these materials are soft, high energy is required to strip the H atoms from the ABH$_4$ matrix owing to the strong covalent bonding between H and B in the [BH$_4$]$^-$ complex.

### 3.2. Density of states

The calculated total density of states (DOS) at the ground-state equilibrium volumes for the ABH$_4$ series is displayed in Fig. 3. All these compounds have finite energy gaps between the valence (VB) and conduction bands. Hence, they are proper insulators with estimated band gap between 5.5 (CsBH$_4$) and 7.0 eV (LiBH$_4$). The large band gap is a feature which the ABH$_4$ series has in common with the AAlH$_4$ and AGaH$_4$ series (all members of the latter series have band gaps of ~5 eV [31]). The calculated band gap of the AAlH$_4$ and AGaH$_4$ series appears to be invariant whereas that for ABH$_4$ series varies almost linearly with the size of A$^+$. Also the width of the bands (in particular the VB) varies nearly linear with the size of A$^+$. The band-width narrowing from LiBH$_4$ to CsBH$_4$ reflects the enhanced A–B and A–H bond strength.
along the series [the A-B and A-H bond lengths vary almost linearly with the size of A⁺ whereas the B-H separations are nearly constant (see above) and all H-H separation exceeds 2 Å].

In the total DOS of LiBH₄ (Fig. 4) the VB is split into separate regions (region I: −6.9 to −5.7 eV, region II: −2.1 to Eₓ) with a ca. 3.6 eV gap between these regions. B-s states are mainly found in region I. The total DOS in region II is contributed by B-p, H-s, Li-s, and Li-p states. In general the B-s and p-states are well separated whereas the Li-s and p states mainly appear in region II. The B-p and H-states are energetically degenerate in region II, which clearly facilitates the formation of the hybridization prerequisite for the occurrence of the covalently bonded [BH₄]⁻ complex of the structure. The site-projected DOS (Fig. 4) shows that (as expected) the Li atoms contributed to the bonding by donating electron to the [BH₄]⁻ complex and become ionized to Li⁺. In order to further illustrate this scenario Fig. 5 displays the energy-projected charge density (i.e. the charge-density distribution of the electrons in the energy range −2.1 to Eₓ). The [BH₄]⁻ units take the form of well separated molecular species distributed over the Li lattice with almost charge depleted regions (near zero electron density) between the lithium and the complex unit, viz. in conformity with the ion picture of Li⁺ and [BH₄]⁻. Within the [BH₄]⁻ complex the predominantly covalent nature of the bonding between B and H is further confirmed by the charge distribution between these atoms. The H-s electrons are tightly bond to the B-p states, and the characteristic sp³ hybridization occurs within the [BH₄]⁻ complex.

4. Conclusion

The low-temperature crystal structures of the entire ABH₄ (A = Li–Cs) series have been investigated using density-functional total-energy calculations. On moving from Li to Cs in the series the atomic arrangements are systematically changed from lower- to higher-symmetric structures. The theoretically derived unit-cell parameters and atomic coordinates for LiBH₄ are in reasonable agreement with the experimental findings. However, the calculations show an almost ideal tetrahedral configuration for the [BH₄]⁻ complex, whereas experimental studies suggest appreciable distortion. For the compounds with A = K, Rb, and Cs the theoretically derived structures deviate from the low-temperature experimental findings. Theory predicts that the low-temperature structures of KBH₄ and RBH₄ stabilize in the β-NaBH₄-type structure and CsBH₄ stabilizes in the β-KBH₄-type structure. The calculated total-energy survey for possible structures suggests that these ABH₄ compounds are sensitive to temperature, and stabilization of metastable phases is considered very likely. The theoretically derived unit-cell dimensions and atom coordinates for the metastable phases are discussed in relation to the experimental knowledge. The calculated bulk moduli suggest that the ABH₄ compounds should be easily compressible. From the partial DOS and charge-density analyses it is concluded that the compounds have strong covalent interaction between B and H in the [BH₄]⁻ complex and ionic bonding character between [BH₄]⁻ and A⁺. The ABH₄ compounds exhibit finite band gaps between the valence and conduction bands, and according to the size of the band gaps the compounds are classified as wide band-gap insulators.

Acknowledgments

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Note added in proof

The experimental data listed for β-KBH₄ in Table 1 are quoted from the on-line in-press version of Ref. [24]. In the actually printed version of Ref. [24] the space group of the phase in question has been changed to P4₂/mmc and the quoted data in Table 1 therefore really refer to γ-KBH₄. So, both the theory and experimental findings agree very well.

References

Chemical-bonding and high-pressure studies on hydrogen-storage materials

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Abstract

From gradient-corrected, all-electron, full-potential, density-functional calculations, including structural relaxation, it is shown that the metal-hydride series $RT\text{InH}_{1.33}$ ($R = \text{La, Ce, Pr, or Nd}; T = \text{Ni, Pd, or Pt}$) violate the "2-$A$" rule as well as the hole-size requirement. These hydrides possess unusually short H–H separations which in the most extreme case for LaPtInH$_{1.33}$ is as short as 1.454 Å. These findings have been analyzed in terms of charge density, charge transfer, electron-localization function, crystal-orbital Hamilton population, and density of states analyses. From high-pressure studies it is predicted several successive pressure-induced structural transitions in MgH$_2$ within the 20 GPa range. Calculations have also shown several pressure-induced structural transitions in alkali aluminum tetrahydrides with large volume reductions at the phase-transition points and small energy differences between the ambient-pressure and subsequent high-pressure phases.

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Keywords: Hydrogen-storage materials; Chemical bonding; Electronic structure; Pressure-induced structural transition; Density-functional calculations

1. Introduction

For the usage of hydrogen as the ideal fuel for many types of energy converters one requires efficient and safe storage of hydrogen in the form of metal hydrides. Over the past few decades, a major challenge which still remains, is to identify optimal intermetallics for such purposes. Rare-earth alloys seem promising owing to a high hydrogen capacity per volume unit and an ability to absorb hydrogen under moderate conditions [1,2]. The hydrogen absorption/desorption properties of these alloys are very much dependent on the constituents and the metal–hydrogen bonding interactions will play a major role for the stability of the hydrides. In order to optimize hydride phases for a certain application, an improved understanding of the role of individual alloy constituents in relation to hydrogen and the subsequent influence on electronic and structural properties are desirable.

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The crystal structures of intermetallic phases are often complex and there are several potential interstices that might accommodate the hydrogen depending on factors like the size and shape of the interstitial site, chemical nature of the surrounding atoms, and the interatomic distances to hydrogen and the coordinating atoms [3,4]. Structural studies of intermetallic hydrides have revealed that empirical rules can be used to predict important features of the hydrogen sublattices in a given metal matrix [5,6]. The search for efficient hydrogen-storage metal hydrides has some extent been hampered by the mental barriers which empirical rules have put on the thinking. For example, the radius of the interstitial hole which hydrogen is expected to occupy should be >0.4 Å. A survey [6] of stable hydrides shows that the minimum H–H distance exceeds 2.1 Å (the “2-Å rule”). This empirical pattern is later [7] supported by band-structure calculations which ascribe the features to repulsive interaction generated by the partially charged hydrogen atoms. A practical consequence of this repulsive H–H interaction in metal hydrides is that it puts a limit to the amount of hydrogen which can be accommodated within a given structural framework. So, if H–H separations less than 2 Å would be possible this could open for new prospects for potential candidates with higher hydrogen-storage capacity.

The non-metallic, complex hydride K$_2$ReH$_9$ [8,9] appears to provide a good example of violation of “2-Å rule”, with an H–H separation of 1.87 Å and experimental [10] and theoretical [11] results for Th$_2$AlH$_4$ agree on a closest H–H separation of around 1.95 Å. The recent experimental findings [12] for deuterides based on a ZrNiAl-type matrix (LaNiInD$_{1.23}$, CeNiInD$_{1.26}$, and NdNiInD$_{1.192}$) prove that even short D–D distances of about 1.5–1.6 Å are indeed possible and thus a striking violation of the “2-Å rule” is noted. Two explanations have been proposed. First, pairing of the hydrogen atoms (either by molecular H$_2$-like bonding or by bonding mediated by the intermediate T atom) has been advanced to explain the anomalous NMR spectrum of CeNiInH$_{1.0}$ [13]. The second explanation focuses on the significantly shorter La–La distance in LaNiInH$_{1.33}$ than in closely related phases [12], whereby the La atoms (more generally R) may act as a shielding that compensates the repulsive interaction between the H atoms. The hydrogen–metal interaction in transition-metal hydrides is less clear, and even the charge on the hydrogen in these materials has been under dispute. Using first-principle density-functional calculations we have analyzed bonding behavior in this novel class of materials.

Hydrides for hydrogen storage need to be able to form hydrides with a high hydrogen-to-metal ratio, but should not be too stable, so that the hydrogen can easily be released without excessive heating. The hydride, MgH$_2$, can store up to 7 wt.% of hydrogen whereas the automobile industry has set 5 wt.% as a target. There are problems in using MgH$_2$ for practical applications such as: (1) The rate at which hydrogen absorbs and desorbs is too low because diffusion of the hydrogen through the hydride lattice is slow. (2) On loading the hydrogen molecules do not readily dissociate at the surface of Mg to generate the atomic hydrogen that must diffuse into the lattice to form a bulk hydride phase. (3) The enthalpy of formation of MgH$_2$ is too large, so that the hydride needs to be heated to around 350 °C to release the hydrogen gas at ambient pressure [14]. So, to understand the stability of metal hydrides is a key to rationally investigate and design potential hydrogen-storage materials. Further, theoretical high-pressure studies on metal hydrides assumes additional importance as the high-pressure X-ray and neutron diffraction studies have difficulties to establish the positions of hydrogen (deuterium) atoms.

In the first part of this paper we present analyses of chemical bonding in selected metal hydrides with the help of partial density of states (DOS), crystal-orbital Hamilton population (COHP), charge density, charge difference and electron-localization function. The second part deals with the structural stability of these materials at high-pressures based on total-energy studies.

2. Computational details

The generalized-gradient approximation (GGA) generally gives good equilibrium volume
and cohesive energy and hence we have used the GGA [15] for all the ab initio calculations to obtain structural parameters and total energies for each of the particular structural arrangements considered. The structures are fully relaxed for all volumes considered in the present calculations using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. The full-potential linear muffin-tin orbital (FP-LMTO) [16] and the projected augmented wave (PAW) implementation of the Vienna ab initio simulation package (VASP) [17] were used for the total-energy calculations to establish phase stability and transition pressures. Both methods yielded nearly the same result, e.g., the transition pressure from $\alpha$- to $\gamma$-MgH$_2$ came out as 0.385 and 0.387 GPa from FP-LMTO and VASP, respectively. Similarly almost identical values were obtained for ground-state properties like bulk modulus and equilibrium volume. Hence, except for purposely duplicated test calculations we used only the VASP code because of its computational efficiency. In order to avoid ambiguities regarding the free-energy results we have always used the same energy cutoff and a similar $k$-grid density for convergence. In all calculations 500 $k$ points in the whole Brillouin zone were used for $\alpha$-MgH$_2$ and a similar density of $k$ points for the other structural arrangements. The PAW pseudo-potentials [18] were used for all our VASP calculations. A criterion of at least 0.01 meV atom$^{-1}$ was placed on the self-consistent convergence of the total energy, and the calculations reported here used a plane wave cutoff of 400 eV. The present type of theoretical approach has recently been successfully applied [19,20] to reproduce ambient- and high-pressure phases computationally.

3. Results and discussion

3.1. Partial densities of states

In order to analyze the bonding interactions between the constituents of the intermetallic matrix and the mutual perturbation with hydrogen, the calculated partial DOS curves for LaPdIn and

![Fig. 1. The calculated angular-momentum-projected density of states for LaPdIn and LaPdInH$_{1.33}$ obtained from FLMT0 calculations. Fermi level is set to zero and marked by the vertical line.](image)

LaPdInH$_{1.33}$ are given in Fig. 1. The presence of finite DOS at $E_F$ for both the intermetallic matrix and the hydride indicate that both phases are in a metallic state. The relatively small amount of electrons present in the valence band region for the La site in the unhydrated matrix indicates a degree of ionic bonding between La and the other constituents. The addition of hydrogen reduces the valence electron distribution at the La site due to the transfer of electrons from La to hydrogen. The energetically degenerate nature of Pd-4d and In-5p electrons in the valence band indicate the presence of covalent bonding between these atoms. Owing to different chemical environment of Pd in (1b) and (2c) sites, the DOS features are considerably different. In particular the Pd-5s electrons are quite localized at Pd(1b) compared with that in Pd(2c). The introduction of hydrogen perturbs strongly the valence band of Pd(2c) and in particular broad
Electronic states are induced in the lower energy region of the VB. In-5s electrons occurring as a single broad band in LaInPd are separated into two narrow states in LaPdInH\textsubscript{1.333}. The transfer of electrons from the host lattice to the hydrogen makes the s electrons at the hydrogen site well localized.

### 3.2. Crystal-orbital Hamilton-population analysis

To gauge the bond strength we have used crystal-orbital Hamilton-population COHP analyses, as is implemented in the TBLMTO-47 package [21]. The COHP (viz. the Hamiltonian-population-weighted DOS) is identical with the crystal-orbital-overlap population. Ideally the COHP takes a negative value for bonding and positive for antibonding states. In order to illustrate the bond strength between the constituents the COHP between atoms in LaPdInH\textsubscript{1.333} is shown in Fig. 2 taking all valence orbitals into account. From this illustration it seems clear that the strongest bond in LaPdInH\textsubscript{1.333} is between Pd and H. There is considerable covalent interaction between Pd(2c) and In. There are both bonding and antibonding states present in the COHP between the H atoms in the VB and hence the bonding interaction between the H atoms may be considered as weak. When one includes hydrogen in the LaPdIn matrix the estimated integrated crystal-orbital Hamilton population [22] for the Pd–In bond is reduced from ca. 1.1 to 0.75 eV. This appears to reflect transfer of electrons from both Pd and In to the H site which reduces the covalent interaction between Pd and In upon hydrogenation.

### 3.3. Charge density, charge difference, and ELF

In order to improve the understanding about the bonding interactions, the calculated valence–charge-density distribution in (1 0 0) of LaPdInH\textsubscript{1.333} is depicted in Fig. 3a. The impression from this illustration appears to be that Pd and H form an PdH\textsubscript{2} molecule-like structural subunits. Moreover, Fig. 3a demonstrates that there is no substantial charge density distributed between the H atoms. In order to depict the role of charge transfer we have displayed the charge transfer (the difference in the electron density of the compound and that of constituent atoms superimposed on the lattice grid) for LaPdInH\textsubscript{1.333} within (1 0 0) in Fig. 3b. From Fig. 3b it is clear that electrons are transferred from La, In, and Pd to the H site. So, there is a strong ionic bonding component between H and the metallic host lattice. The repulsive interaction between the negatively charged H atoms could explain why the H–H separation in these materials are larger than that in the H\textsubscript{2} molecule. The ELF is an informative tool to distinguish different bonding interactions in solids [23], and the ELF for LaPdInH\textsubscript{1.333} in (1 0 0) is given in Fig. 3c. The large value of the ELF at the H site indicates strongly paired electrons with local bosonic character. The negligibly small ELF between Pd and H indicates that the probability of finding parallel spin electrons close together in this region is rather high (correspondingly small for antiparallel spin pairs) and the detailed analysis show that delocalized metallic Pd(2c)-d electrons are distributed in this region. Even though the charge distribution between Pd and H suggests a typical covalent bonding this false impression...
originates from the influence of non-bonding Pd-$d$ electrons. Hence, chemical bonding between Pd and H is dominated by ionic components with considerable metallic weft. The partial DOS analysis also show that the H-s states are well separated from the Pd-$d$ states in the whole VB indicating (see Fig. 1) the presence of ionic bonding between Pd and H. Due to the repulsive interaction between the negatively charged H atoms, the ELF contours are not spherically shaped but polarized toward La and In. The localized nature of the electrons at the H site and their polarization toward La and In reduce significantly the H–H repulsive interaction and this can explain the unusually short H–H separation in this compound. The ELF between the H atom takes a significant value of 0.35, and considering the small charge density, this indicates a weak metallic type of interaction between the hydrogen atoms.

The bond connecting two hydrogen atoms within the R$_3$Pd$_2$ trigonal–bipyramidal is surrounded by three R atoms. When the La–H separation is reduced the H atoms are allowed to approach each other more closely and if the La–H separation is increased then the equilibrium H–H separation also increased. The considerable changes in the equilibrium H–H distance on the tested $R$ displacements [24] indicate that La in the La$_3$Pd$_2$ trigonal–bipyramidal configuration acts as a shielding that to some extent compensates the repulsive H–H interactions. The detailed bonding analysis show that the paired, localized, and bosonic nature of the electron distribution at the H site are polarized toward La and In which reduces the repulsive interaction between the negatively charged H atoms. We have shown that the short distances between the H atoms in such metal hydrides are governed primarily by the polarization of negative charges on H toward the electropositive La and In.

3.4. High-pressure studies on metal hydrides

LiAlH$_4$ crystallizes in the monoclinic $\alpha$-LiAlH$_4$-type structure with space group $P2_1/c$ and four formula units per unit cell [25]. In agreement with the experimental observations we found that the lowest energy configuration among the seven considered possibilities for LiAlH$_4$ is the already established ambient pressure/temperature $\alpha$-LiAlH$_4$-type structure (Fig. 4). We have identified two potential high-pressure modifications of LiAlH$_4$: At 2.6 GPa $\alpha$-LiAlH$_4$ (prototype structure) transforms to $\beta$-LiAlH$_4$ ($\alpha$-NaAlH$_4$ type) and a subsequent transition from $\beta$- to $\gamma$-LiAlH$_4$ (KGaH$_4$ type) is established at 33.8 GPa. The important aspect of the $\alpha$-to-$\beta$ transition in LiAlH$_4$ is the small energy difference (see inset in Fig. 4) between the involved phases (only 11.56 meV f.u.$^{-1}$, or 1.154 kJ mol$^{-1}$, which is indeed much smaller than that found for other hydrides [26] and oxides [27]. At the $\alpha$-to-$\beta$ transition point for LiAlH$_4$, the estimated difference in cell volume is ca. 17% (Fig. 6) [28]. The Raman scattering measurement on the high-pressure phase also indicates the
Magnesium is an attractive material for hydrogen-storage applications because of its light weight, low manufacture cost and high hydrogen-storage capacity (7.66 wt.%). \( \alpha \)-MgH\(_2\) crystallizes with the \( \text{TiO}_2 \)-\( \gamma \)-type \(( \gamma = \text{rutile} \) structure at ambient pressure and low temperature \([30,31]\). At higher temperatures and pressures tetragonal \( \alpha \)\-MgH\(_2\) transforms into orthorhombic \( \gamma \)\-MgH\(_2\). Recently Bortz et al. \([32]\) solved the crystal structure of \( \gamma \)\-MgH\(_2\) (\( \alpha \)-PbO\(_2\) type) on the basis of powder neutron diffraction data collected at 2 GPa. The \( \alpha \)-to \( \gamma \)-MgH\(_2\) transition pressure is not yet known. In addition to the experimentally identified \( \alpha \)- and \( \gamma \)-modifications of MgH\(_2\), we have carried out calculations for nine other possible \([27]\) types of structural arrangements for MgH\(_2\). The calculated total energy vs. cell volume relation for all these alternatives are shown in Fig. 5. The equilibrium volumes, (30.64 and 30.14 \( \text{Å}^3 \)\,f.u.\(^{-1}\)) for \( \alpha \)- and \( \gamma \)-MgH\(_2\), respectively, are within 1\% of the experimental values indicating that the theoretical calculations are reliable. The calculated transition pressure for the \( \alpha \)-to \( \gamma \)-MgH\(_2\) conversion is 0.387 GPa (Fig. 6) and as the free energy of the two modification is nearly the same at the equilibrium volume, it is only natural that these phases coexist in a certain volume range \([32]\).

The subsequent phase transition from \( \gamma \)-to \( \beta \)-MgH\(_2\) occur at 3.84 GPa. Bortz et al. \([32]\) found no evidence for the formation of such a \( \beta \) modification up to 2 GPa, whereas Bastide et al. \([30]\) found that at higher pressure (4 GPa) and temperature (923 K) there occurs a new phase (viz. \( \beta \) in accordance with our findings). The volume discontinuity at the \( \gamma \)-to-\( \beta \) transition point is 1.45 \( \text{Å}^3 \)\,f.u.\(^{-1}\). On further increase of the pressure to around 6.7 GPa \( \beta \)-MgH\(_2\) is predicted to transform into \( \delta \)-MgH\(_2\) (orthorhombic Pbc\(_2\)) with a volume collapse of 1.1 \( \text{Å}^3 \)\,f.u.\(^{-1}\). In the pressure range 6.7–10.2 GPa the modifications with structural arrangements of the types \( \beta \)-MgH\(_2\), \( \epsilon \)-MgH\(_2\) and \( \delta \)-MgH\(_2\) are seen to lie within a narrow energy range of some 10 meV (Fig. 5). This closeness in energy suggests that the relative appearance of these modification will be quite sensitive to, and easily affected by, other external factors like temperature and remnant lattice stresses. A transformation to \( \epsilon \)-MgH\(_2\) (AlAu\(_2\)-type structure; also called cotun-

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**Fig. 4. Total energy vs. volume curve for LiAlH\(_4\), for different possible structural arrangements.** The inset shows the relationship for \( \alpha \)- and \( \beta \)-LiAlH\(_4\) near their equilibrium volume. The points ‘a’ and ‘b’ with arrows indicate the total energy cross-over point where the structural transition takes place.

The subsequent phase transition from \( \gamma \)-to \( \beta \)-LiAlH\(_4\) near their equilibrium volume, it is only natural that these phases coexist in a certain volume range \([32]\). The conditions at the transition point between the \( \alpha \) and \( \beta \)-LiAlH\(_4\) show an even larger volume difference (viz. a huge value of 22\%), which to our knowledge is the first establishment of such huge volume change at a transition point in hydrides. For example, in NaAlH\(_4\) the calculated volume difference at the transition point between the \( \alpha \) and \( \beta \)-LiAlH\(_4\) almost the same volume at the \( \beta \)-to-\( \gamma \) transition point. The relatively small equilibrium volume of \( \beta \)-LiAlH\(_4\) along with its high weight content of hydrogen imply an increased hydrogen-storage capacity and therefore it would be of interest to explore the possibility of stabilizing this phase by chemical means, and perhaps also find a way to improve the kinetics of the reversible hydrogen absorption/desorption because the bonding behavior of the \( \beta \) phase is drastically different from the \( \alpha \) phase.
structural transition in a narrow pressure range. It is interesting to note that our recent experimental high-pressure studies with synchrotron radiation appear to confirm the theoretical prediction.

Calculated equation of states data for alkali aluminohydrides and alkaline-earth hydrides obtained by the VASP-PAW method are shown in Fig. 6. When the cation radius is small we find several pressure-induced structural transition in such materials. For example we find two pressure-induced structural transition in LiAlH$_4$ (i.e., α-to-β and β-to-γ), only one transition in NaAlH$_4$ and there appears to no high-pressure phase transition in KAIH$_4$ up to 100 GPa. Further, it is interesting to note that there is huge volume collapse at the first phase-transition points in materials which comprises small cations. The implication for the pressure-induced volume collapse is that one can store more hydrogen in a smaller volume in such a high-pressure phase than in the ambient-pressure modification. This abnormal behavior is associated with an electronic transition from Al-$s$ to -$p$ states. The high wt.% of hydrogen, around 22% smaller equilibrium volume, and the drastically different bonding behavior compared with the α phase (which also may improve the kinetics) indicate that β-LiAlH$_4$ could be a potential hydrogen-storage material.

Similar to alkali aluminohydrides alkaline-earth hydrides with low cation radii also exhibit a huge volume collapse at the first pressure-induced structural transition (see also Fig. 6). MgH$_2$ is the first metal hydride found to exhibit several pressure-induced
phase-transition point. Application of pressure transforms $\alpha$- to $\beta$-BeH$_2$ at 7.07 GPa with a calculated volume discontinuity at the transition point of ca. 19.2\% (ca. 26.4\% equilibrium volume difference) and an energy difference of $\sim$0.4 eV. Such a huge pressure-induced volume collapse is rather uncommon among hydrides as well as inorganic compounds in general. However, large volume collapses (9–20\%) under pressure are observed for lanthanides and actinides associated with the valence transition or localized-to-delocalized transition of $f$ electrons in these systems. Like alkali aluminohydrides, we observed several pressure-induced structural transition for alkaline-earth hydrides with small cation. For BeH$_2$ and MgH$_2$ we have found four pressure-induced structural transitions whereas only one pressure-induced structural transition were observed for BaH$_2$. From these systematic studies it appears that if the ionic radius of the cation is small one can expect several pressure-induced structural transitions in main group metal hydrides and a particularly huge volume collapse at the first phase transition.

Industries are looking for hydrogen-storage materials with high wt.% of hydrogen and good hydrogen absorption/desorption kinetics. The existing phases lack one or both of them. One strategy is to find possible metastable phases in potential hydrides and try to stabilize them by suitable thermo/chemical processing conditions. High-pressure study is one way to identify possible metastable phases in solids. From our high-pressure studies we identified several high-pressure phases in these materials and in particular we found large volume collapse at the first phase-transition point in several potential hydrogen-storage materials. Also, the chemical bonding behavior of these high-pressure phases are drastically different from that of ambient-pressure phase and hence it is expected that the metastable phases may improve the hydrogen absorption/desorption kinetics.

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References


New High-pressure Phases of Lithium and Sodium Aluminum Tetrahydrides and their Implications to Hydrogen Storage

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Abstract
A systematic high-pressure study on LiAlH$_4$ and NaAlH$_4$ has been carried out using density-functional total-energy calculations. From the theoretical simulations, it is found that both LiAlH$_4$ and NaAlH$_4$ are subject to structural phase transitions at high pressure. $\alpha$-LiAlH$_4$ transforms to $\beta$-LiAlH$_4$ ($\alpha$-NaAlH$_4$-type structure) at 2.6 GPa with a huge volume collapse of ca. 22 \% (according to equilibrium volumes) higher than ever observed among hydrides. This unusual behaviour is associated with an electronic conversion from Al-$s$ to $p$ states. At 33.8 GPa, LiAlH$_4$ is predicted to undergo a $\beta$-to-$\gamma$ transition from $\alpha$-NaAlH$_4$- to KGaH$_4$-type structure. $\alpha$-NaAlH$_4$ converts to $\beta$-NaAlH$_4$ (SrMgH$_4$-type structure) at 6.4 GPa with a 4\% volume contraction. The high-pressure $\beta$ phases of both compounds would store hydrogen more volume efficient than the corresponding $\alpha$ phases. The calculated electronic structures of these materials at ambient and elevated pressures indicate that all phases have a nonmetallic character. The calculated band gap for $\beta$-NaAlH$_4$ is almost half of that for the $\alpha$ phase, whereas the band gaps for $\alpha$- and $\beta$-LiAlH$_4$ are nearly same.

Keywords: High pressure study. Structural stability. Crystal structure. Lithium aluminum tetrahydride. Sodium aluminum tetrahydride.

Introduction
Introduction of “Hydrogen Economy” requires safe and efficient storage of hydrogen, and hence potential solid storage materials have been intensively studied for several decades. The enormous potential for fuel cells have created a renewed interest in metal hydrides as efficient materials for reversible hydrogen storage. The hitherto known hydrides with high capacity for potential reversible hydrogen storage are hampered by thermodynamic and/or kinetic limitations. Interstitial (metal) hydrides are easily reversible around room temperature, but the relative weight of the stored hydrogen is relatively low (1.5 to 2.5 wt.\%) [1,2]. In contrast, MgH$_2$ and LiH have relatively high weight contents of hydrogen (7–13 wt.%), but owing to the presence of strong ionic/covalent bonding interactions, the desorption temperatures are high (> 250° C).

Recent interest has been directed toward ternary aluminum hydrides owing to their enhanced storage capacity (e.g., LiAlH$_4$ and NaAlH$_4$ with 10.6 and 7.5 wt.% theoretical hydrogen content, respectively) as solid-state sources for hydrogen storage (e.g., fuel reservoirs) etc. Hence, LiAlH$_4$ and NaAlH$_4$ could be viable candidates for practical usage as on-board-hydrogen-storage materials. However, a serious problem with these materials is poor
kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Improved understanding of the processes which occur in these hydrogen-containing materials during uptake and release of hydrogen are of considerable interest. Recent experimental evidences show that LiAlH₄ and NaAlH₄ rapidly release 7.9 and 5.6 wt.% of the maximum stored hydrogen, respectively, after being subjected to mechano-chemical processing under ambient conditions and with the presence of certain transition-metal catalysts [3-6]. Hence, the identification of possible metastable phases of these materials will be of fundamental interest.

In particular theoretical investigations of LiAlH₄ and NaAlH₄ assumes additional importance as high-pressure X-ray and neutron diffraction studies will experience difficulties in identifying more accurate positions for the hydrogen atoms. The present study concerns phase stabilities and electronic structures of LiAlH₄ and NaAlH₄ as explored by first-principle ab initio calculations.

**Computational method**

Total energies have been calculated using the projected-augmented plane-wave (PAW) [7] implementation of the Vienna ab initio simulation package (VASP) [8]. Since it is generally found that the generalized-gradient approximation (GGA) [9] gives better equilibrium structural parameters and cohesive energies than alternative computational approaches we have used GGA for all calculations reported in this communication. The structures were fully relaxed for all volumes considered in the present calculations using force as well as stress minimization. Experimentally established structural data were used as input for the calculations when available. For α-LiAlH₄ and α-NaAlH₄ we have used 500 and 432 k points.

![Figure 1. Crystal structure of (a) α-LiAlH₄ (prototype; monoclinic, P2₁/c) (b) β-LiAlH₄ / α-NaAlH₄ (α-NaAlH₄; tetragonal, I4₁/a; isostructural atomic arrangement) and (c) β-NaAlH₄ (SrMgH₄-type; orthorhombic, Cmc2₁).](image-url)
respectively, in the whole Brillouin zone. In order to avoid ambiguities regarding the free-energy results we have always used the same energy cut-off and k-grid densities for all the structural configurations considered in the present calculations. A criterion of at least 0.01 meV/atom was placed on the self-consistent convergence of the total energy, and the calculations reported here used a plane wave cut-off of 600 eV. Seven closely related structure types have been considered for the present theoretical modelling, viz. \( \alpha \)-LiAlH\(_4\) (monoclinic; \( P2_1/c \)), \( \alpha \)-NaAlH\(_4\) (tetragonal; \( I4_1/a \)) \( \beta \)-LiBH\(_4\) (hexagonal; \( P6_3/mc \)) NaGaH\(_4\) (orthorhombic; \( Cmcm \)), NaBH\(_4\) (cubic; \( Fm\overline{3}m \)), SrMgH\(_4\) (orthorhombic; \( Cmc2_1 \)), and KGaH\(_4\) (orthorhombic; \( Pnma \)) [10].

Table 1. Optimized structural parameters for LiAlH\(_4\) and NaAlH\(_4\) in the actual structural arrangements deduced computationally.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Unit-cell dimensions(^a)</th>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-LiAlH(_4) (prototype; ( P2_1/c ))</td>
<td>( a = 4.8535 ) (4.8174)(^b)</td>
<td>Li : 0.5699, 0.4652, 0.8245 (0.5603, 0.4656, 0.8266);(^b)</td>
</tr>
<tr>
<td></td>
<td>( b = 7.8259 ) (7.8020)(^b)</td>
<td>Al : 0.1381, 0.2017, 0.9319 (0.1386, 0.2033, 0.9302);(^b)</td>
</tr>
<tr>
<td></td>
<td>( c = 7.8419 ) (7.8214)(^b)</td>
<td>H1 : 0.1807, 0.0986, 0.7630 (0.1826, 0.0958, 0.7630);(^b)</td>
</tr>
<tr>
<td></td>
<td>( \beta = 111.878 ) (112.228)(^b)</td>
<td>H2 : 0.3542, 0.3723, 0.9777 (0.3524, 0.3713, 0.9749);(^b)</td>
</tr>
<tr>
<td></td>
<td>( a = 4.6611 ) (4.7312)(^b)</td>
<td>H3 : 0.2361, 0.0810, 0.1146 (0.2425, 0.0806, 0.1148);(^b)</td>
</tr>
<tr>
<td></td>
<td>( c = 10.5219 ) (10.7161)(^b)</td>
<td>H4 : 0.7948, 0.2633, 0.8717 (0.7994, 0.2649, 0.8724);(^b)</td>
</tr>
<tr>
<td>( \beta )-LiAlH(_4) (( \alpha )-NaAlH(_4)-type; ( I4_1/a ))</td>
<td>( a = 4.6611 ) (4.7312)(^b)</td>
<td>Li : 0, 1/4, 5/8; Al : 0, 1/4, 1/8;</td>
</tr>
<tr>
<td></td>
<td>( c = 10.5219 ) (10.7161)(^b)</td>
<td>H : 0.2527, 0.4237, 0.5413 (0.2492, 0.4191, 0.5429);(^b)</td>
</tr>
<tr>
<td>( \gamma )-LiAlH(_4) (KGaH(_4)-type; ( Pnma ))</td>
<td>( a = 6.4667 ) (5.4421)(^b)</td>
<td>Li : 0.2428, 1/4, 0.2467 (0.2497, 1/4, 0.2502);(^b)</td>
</tr>
<tr>
<td></td>
<td>( b = 5.3478 ) (4.8483)(^b)</td>
<td>Al : 0.5120, 1/4, 0.8221 (0.5002, 1/4, 0.7361);(^b)</td>
</tr>
<tr>
<td></td>
<td>( c = 11.0828 ) (11.1483)(^b)</td>
<td>H1 : 0.3067, 1/4, 0.9617 (0.2941, 1/4, 0.9617);(^b)</td>
</tr>
<tr>
<td></td>
<td>( a = 4.9965 ) (4.9801)(^b)</td>
<td>H2 : 0.7162, 1/4, 0.9631 (0.7189, 1/4, 0.9467);(^b)</td>
</tr>
<tr>
<td></td>
<td>( c = 11.0828 ) (11.1483)(^b)</td>
<td>H3 : 0.4889, 0.9833, 0.2943 (0.4998, 0.9173, 0.3279);(^b)</td>
</tr>
<tr>
<td>( \alpha )-NaAlH(_4) (prototype; ( I4_1/a ))</td>
<td>( a = 4.599 ) (4.9801)(^b)</td>
<td>Na : 0, 1/4, 1/8; Al : 0, 1/4, 5/8;</td>
</tr>
<tr>
<td></td>
<td>( c = 11.0828 ) (11.1483)(^b)</td>
<td>H : 0.2199, 0.3710, 0.5639 (0.2372, 0.3869, 0.5456);(^b)</td>
</tr>
<tr>
<td>( \beta )-NaAlH(_4) (SrMgH(_4)-type; ( Cmcm2_1 ))</td>
<td>( a = 3.5493 ) (3.4047)(^b)</td>
<td>Na : 0, 0.1708, 0.2373 (0, 0.1695, 0.2409);(^c)</td>
</tr>
<tr>
<td></td>
<td>( b = 13.8304 ) (12.9950)(^b)</td>
<td>Al : 0, 0.4147, 0.2056 (0, 0.4139, 0.2047);(^c)</td>
</tr>
<tr>
<td></td>
<td>( c = 5.1133 ) (5.0746)(^b)</td>
<td>H1 : 0.3485, 0.4807 (0.3476, 0.4877);(^c)</td>
</tr>
<tr>
<td></td>
<td>( a = 3.5493 ) (3.4047)(^b)</td>
<td>H2 : 0, 0.3147, 0.0117 (0, 0.3105, 0.0116);(^c)</td>
</tr>
<tr>
<td></td>
<td>( c = 5.1133 ) (5.0746)(^b)</td>
<td>H3 : 0.0763, 0.6842 (0.0751, 0.6811);(^c)</td>
</tr>
<tr>
<td></td>
<td>( c = 5.1133 ) (5.0746)(^b)</td>
<td>H4 : 0, 0.5232, 0.3816 (0, 0.5269, 0.3739);(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Axes in Å and angles in °. \(^b\) Experimental value from Ref. 11. \(^c\) Calculated value at equilibrium. \(^d\) Calculated value at transition point. \(^e\) Experimental value from Ref. 13.

Structural aspects

LiAlH\(_4\) crystallizes in the monoclinic \( \alpha \)-LiAlH\(_4\)-type structure (see Figure 1a) with four formula units per unit cell [11]. Four hydrogen atoms are arranged around aluminum in an
almost regular tetrahedral configuration. The structure consists of [AlH$_4$]$^-$ units well separated by Li$^+$ ions (Figure 1a). The Al–H distances vary between 1.592 and 1.641 Å, the Li–H separations between 1.831 and 1.974 Å, and the arrangement of the lithium ions gives rise to one relatively short Li–Li distance of ca. 3.1 Å.

Under ambient conditions NaAlH$_4$ crystallizes in the tetragonal structure shown in Figure 1b [12,13]. The [AlH$_4$]$^-$ anion has a compressed tetrahedral shape with Al–H distances of 1.603 Å. The Na$^+$ cation has eight nearest H neighbours which define the vertices of a distorted triangular dodecahedron.

**Results and discussion**

In order to gain insight into the structural stability of LiAlH$_4$ and NaAlH$_4$, we have adopted the following procedure. First, for each and every structure we have optimized the atomic positions and unit-cell parameters globally using stress and force minimization. Subsequently we varied the unit-cell volume within $\pm$50 and $\pm$15% in steps of 5% and made force and stress minimization for each and every volume globally. The equilibrium volumes were then extracted from the calculated energy vs. volume relationships fitted to the “universal equation of state” proposed by Vinet et al. [14]. In agreement with the experimental findings, the observed ground state structures for both LiAlH$_4$ and NaAlH$_4$ take the lowest energy (Figure 2a,b) among the seven considered alternatives for each compound. Hence, under ambient conditions LiAlH$_4$ and NaAlH$_4$ are confirmed to crystallize in the structural arrangements established experimentally (Figure 2a,b and Table 1). The calculated and experimentally observed unit-cell parameters (Table 1) are within $\pm$1.5% which is well within the state-of-art limit for density-functional calculation, and also the calculated atomic coordinates for α-LiAlH$_4$ and α-NaAlH$_4$ are in good agreement with the experimental findings.

The total-energy calculations for high-pressure conditions show that both compounds should be subject to structural phase transitions at higher pressures. In order to obtain a clearer picture near the structural transition points we have displayed (see inset to Figure 3) the Gibbs free-energy difference (relative to the α-phases) for the pertinent crystal structures of LiAlH$_4$ and NaAlH$_4$ as function of pressure. At 2.6 GPa α-LiAlH$_4$ transforms to β-LiAlH$_4$ (α-NaAlH$_4$-type structure) and a subsequent transition from β-to-γ LiAlH$_4$ (KGaH$_4$-type structure) is established at 33.8 GPa (Figure 3). The experimental high-pressure-temperature study of Bulychev et al. [15] found that the α-to-β transition occurs at a static pressure of 7 GPa and 250–300°C. When the temperature was increased to 500°C, the same study [15] reports that a third LiAlH$_4$ modification occurs (probably the γ modification uncovered by the present calculations). Similarly, α-NaAlH$_4$ transforms to an orthorhombic SrMgH$_4$-type structure at 6.4 GPa.

The co-ordination number (CN) of Al changes from 4 in α-LiAlH$_4$ and α-NaAlH$_4$ to (effectively) 6 in β-NaAlH$_4$ (6 Al–H distances at 1.678–1.864 Å) and γ-LiAlH$_4$ (4 Al–H distances at 1.231–1.360 Å and two further H atoms at some 2.25 Å), which is consistent with the expected general trend of increasing CN with increasing pressure (as a result of the perturbation of the covalent/ionic bonds). The thus established AlH$_6$ coordinations in γ-LiAlH$_4$ is consistent with reported infrared spectra [15]. At the α-to-β transition point for LiAlH$_4$ the
estimated difference in cell volume is ca. 17%. Comparison on the basis of the equilibrium volumes for α- and β-LiAlH₄ show an even larger volume difference of some 22%. To our knowledge this is the first observation of such a large volume collapse at a phase-transition point in hydrides. (The estimated energy difference between the two phases at their equilibrium volume is 11.5 meV f.u.⁻¹.) The calculated volume difference for NaAlH₄ at the transition point between the α and β phases is less than 4% and the involved energy difference of 126 meV f.u.⁻¹ is much higher than for LiAlH₄.

β-LiAlH₄ deserves special attention. The relatively small equilibrium volume of β-LiAlH₄ along with its high weight content of hydrogen imply a promising material with increased hydrogen storage capacity. It would therefore be of interest to explore the possibility of stabilizing this phase by chemical means, and perhaps also find a way to improve the kinetics to facilitate reversible hydrogen absorption/desorption, viz. making use of the drastically different bonding situation in β-LiAlH₄ compared with the α phase. In contrast with the situation at the α-to-β transition point of LiAlH₄ both phases have almost the same cell volume at the β-to-γ transition point. Here we are mainly focussing on the unique features of β-LiAlH₄ and β-NaAlH₄ in relation to the corresponding α-modifications (see also Refs. 10, 16).

Figure 2. Pressure-volume relationship for LiAlH₄ (left) and NaAlH₄ (right). Inset: Gibbs free energy difference with respect to the α-phase in as function of pressure. Arrows mark transition pressures.

The calculated density of states (DOS) of the α and β phases of LiAlH₄ and NaAlH₄ are shown in Figure 3. A common feature of these compounds is their nonmetallic character with finite energy gaps above the Fermi level. For LiAlH₄ both modifications have almost similar band gaps (4.71 eV for α-LiAlH₄ and 4.25 eV for the β-phase; the calculated
band gap of \( \gamma \)-LiAlH\(_4\) being 3.95 eV). On the other hand the estimated band gap for \( \alpha \)-NaAlH\(_4\) is 5.04 eV, which is more than the double of that for \( \beta \)-NaAlH\(_4\) (2.35 eV). The reduced band gap indicates that one on moving from \( \alpha \)- to \( \beta \)-NaAlH\(_4\) weakens the insulating behaviour drastically. In general, metal hydrides have lower decomposition temperature than complex hydrides because of their metallic-type bonding. Assuming that the reduced band gap also reflects a tendency to more metallic character one is led to expect that the decomposition temperature for \( \beta \)-NaAlH\(_4\) is lower than that for the \( \alpha \) phase.

![Graph showing DOS of LiAlH\(_4\) and NaAlH\(_4\)](image)

Figure 3. Calculated total and partial density of states for the \( \alpha \) (at equilibrium) and \( \beta \) modifications of LiAlH\(_4\) and NaAlH\(_4\) (at transition pressure). Fermi levels are set at zero energy and marked by dotted vertical lines; \( s \) states are shaded.

The DOS of the \( \alpha \) and \( \beta \) modification of LiAlH\(_4\) and NaAlH\(_4\) (Figure 3) differ noticeably mainly in the valence band (VB) region. The VB is split into two regions (region I: ca. -6.5 to -4 eV, region II: ca. -3.75 to \( E_F \)) separated by gaps of ca. 0.4 and 0.1 eV in for \( \alpha \)-LiAlH\(_4\), and \( \alpha \)-NaAlH\(_4\), respectively. The reason for the phase transition and the huge volume collapse at the \( \alpha \)-to-\( \beta \) phase transition in LiAlH\(_4\) is hinted from analysis of the partial DOSs. Al-\( s \) states appear mainly in region I. The total DOS in region II is contributed by Al-\( p \), H-\( s \), and Li-\( s \) and -\( p \) states (correspondingly for NaAlH\(_4\)). In general the Al-\( s \) and -\( p \) states are well
separated whereas the Li-\textit{s} and -\textit{p} states appear mainly in region II. The Al-\textit{p} and H-\textit{s} states are energetically degenerate in region II, which clearly facilitates the formation of the hybridization prerequisite for the occurrence of the covalently bonded [AlH\textsubscript{4}]\textsuperscript{−} subunits in the crystal structure (for more details see Ref. 17). When we go from \textit{α} to β-LiAlH\textsubscript{4} (corresponding for NaAlH\textsubscript{4}) the gap in the VB region disappears, which may be taken as a sign of increased hybridization interaction. The changes in the DOSs for Li(Na) are rather insignificant between α- and β-LiAlH\textsubscript{4}(NaAlH\textsubscript{4}) whereas the DOSs for Al is markedly different. In β-LiAlH\textsubscript{4} more mixing of \textit{s} and \textit{p} states are found for the Al site (see the PDOS for Al in Figure 3). The \textit{s}-to-\textit{p} electronic conversion for the Al states in the β-LiAlH\textsubscript{4} appears to be the cause of the huge volume collapse at the \textit{α}-to-β-phase transition.

On going from \textit{α}- to β-LiAlH\textsubscript{4} the width of the VB is increased from ca. 6 to 8 eV, which is partially due to the decrease in the interatomic Al–H, Li(Na)–H, and Li(Na)–Al distances. Due to the enhanced hybridization of Al-\textit{p} with H-\textit{s} at elevated pressure in NaAlH\textsubscript{4}, the Al-\textit{p} peak is shifted from ca. −1.5 eV for α-NaAlH\textsubscript{4} to ca. −3.5 eV for the β phase. This leads to a gain in the band-energy contribution to the total energy with pressure, and this may be the cause of the \textit{α}-to-β phase transition in this case. The reduction in the band gap and the increase in CN for the β modification also provide support for the inferred tendency toward a more metallic nature of the bonding with increasing pressure. This may in turn give rise to appreciably different kinetics for hydrogen absorption/desorption on going from \textit{α} to β-NaAlH\textsubscript{4}.

\textbf{Conclusion}

The \textit{α}-LiAlH\textsubscript{4} and α-NaAlH\textsubscript{4} transform by application of pressure to β modifications at 2.6 and 6.4 GPa, respectively. The estimated volume discontinuity at the \textit{α}-to-β transition point is 17 and 4% for LiAlH\textsubscript{4} and NaAlH\textsubscript{4}, respectively. At higher pressure β-LiAlH\textsubscript{4} transforms further to a γ modification at 33.8 GPa. The coordination number of Al in γ-LiAlH\textsubscript{4} and β-NaAlH\textsubscript{4} is increased from four to six. The electronic density of states confirms that all these phases have a nonmetallic character. The estimated band gap in β-NaAlH\textsubscript{4} is only about half of that in the ambient pressure \textit{α} phase. The involved energy difference between \textit{α}- and β-LiAlH\textsubscript{4} is small and the \textit{α}-to-β transition pressure is also relatively low compared to that for the \textit{α}-to-β transition of NaAlH\textsubscript{4}. The low equilibrium volume for the β phases of LiAlH\textsubscript{4} and NaAlH\textsubscript{4} would imply more efficient storage of hydrogen, and with their relatively high weight content of hydrogen the high-pressure β phases stands out as promising candidates for hydrogen storage. In β-NaAlH\textsubscript{4}, the Al-\textit{p} states are more delocalized and the large DOSs at the top of the VB are moved to lower energies compared with the \textit{α} phase. This leads to a gain in the band-energy contribution to the total energy with pressure, and this may be the reason for the \textit{α}-to-β phase transition in NaAlH\textsubscript{4}.

\textbf{Acknowledgements}

The authors gratefully acknowledge the Research Council of Norway for financial support and the computer time at the Norwegian supercomputer facilities.
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Structural stability and electronic structure for Li$_3$AlH$_6$

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The structural stability and electronic structure of the potential hydrogen-storage material Li$_3$AlH$_6$ has been investigated up to 90 GPa using density-functional total-energy calculations. At ambient conditions Li$_3$AlH$_6$ stabilizes in space group $R\bar{3}$. The structure consists of isolated, close-to-regular [AlH$_3$]$^{1-}$ octahedra, which are connected via six-coordinated Li. We predict that this $\alpha$ phase of Li$_3$AlH$_6$ undergoes three successive structural phase transitions on application of pressure: $\alpha$ to $\beta$ at 18.64 GPa, $\beta$ to $\gamma$ at 28.85 GPa, and $\gamma$ to $\delta$ at 68.79 GPa. All modifications of Li$_3$AlH$_6$ should have nonmetallic character with estimated bandgaps varying between 2.72 and 4.12 eV.

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PACS number(s): 62.50.+p, 61.50.Ks, 61.66.Fn

High-capacity solid-state storage of hydrogen has become increasingly important owing to its use for fuel-cell power generation in automotive and electrical utility applications. The overall hydrogen contents of two alkali-metal aluminohydrides, LiAlH$_4$ and NaAlH$_4$ (10.5 and 7.3 wt. % H$_2$, respectively), are amongst the highest recorded for about 70 known complex hydrides. The temperature induced conversion of lithium aluminohydride (LiAlH$_4$) into lithium hexahydroaluminate (Li$_3$AlH$_6$) has been known for almost three decades. However, the processes occurring in pure LiAlH$_4$ during its thermal decomposition were understood only recently. The decomposition of LiAlH$_4$ takes place in three stages with 5.3 (150–175 °C), 2.6 (180–220 °C), and 2.6 wt. % (above 300 °C) release of H$_2$, respectively:

\[
\begin{align*}
3\text{LiAlH}_4 &\rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2, \\
\text{Li}_3\text{AlH}_6 &\rightarrow 3\text{LiH} + \text{Al} + 3/2\text{H}_2, \\
3\text{LiH} &\rightarrow 2\text{Li} + 3/2\text{H}_2.
\end{align*}
\]

At room temperature, LiAlH$_4$ is unstable relative to Li$_3$AlH$_6$ and the decomposition according to Eq. (1) will occur slowly during storage (around 50% reaction in 10 y). Recently, a significant reduction of the decomposition temperatures for alkali-metal aluminum hydrides doped with appropriate transition metals has been reported. This implies that such hydrides may be possible for practical on-board hydrogen-storage materials for the future, but various basic processing issues must be addressed before the alkali-metal aluminum hydrides and their derivatives will find practical use. With this background, it is natural that Li$_3$AlH$_6$ has obtained appreciable attention.

The crystal structure of Li$_3$AlH$_6$ has up to recently not been completely unraveled and several structure models have been proposed with possible monoclinic (P2$_1$/c, P2$_1$/m, C2/m, Cm, or C2) and rhombohedral (R3, R$\bar{3}$, R$3m$, or R$5m$) space groups. There has been no theoretical attempt to explore the crystal and electronic structures of this compound. However, a fresh experimental study by Brinks and Hauback with combined synchrotron x-ray and neutron diffraction has shown that Li$_3$AlH$_6$ crystallizes in space group R$\bar{3}$. As for other complex hydrides, it is difficult to establish the hydrogen positions from experimental data (even with high-quality x-ray and neutron measurements). In such cases theoretical calculations have proved to be of great help. Insight into the electronic structure and structural stability of Li$_3$AlH$_6$ at high pressure is also of considerable interest in its own right (see above).

It is well established that density-functional calculations are a powerful tool to predict structural properties of materials at ambient and high pressures. The present study considers 21 different types of atomic arrangements with 10–80 atoms per unit cell. Hence, accomplishment of such theoretical simulations demands large computer resources, but the development in the computer technology has made it possible to handle the problem within a reasonable time limit. To the best of our knowledge, a similar approach has so far only been applied for simple compounds with a rather limited number of atoms in the unit cell.

Total energies have been calculated by the projected augmented plane-wave (PAW) implementation of the Vienna $ab$ initio simulation package (VASP). The generalized gradient approximation (GGA) was used to obtain accurate exchange and correlation energies for a particular atomic configuration. All the considered phases were optimized at each volume by force and stress minimization until the Hellmann-Feynman forces are less than 10$^{-3}$ eV/Å. Brillouin-zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. For the $\alpha$-Li$_3$AlH$_6$ structure we used 512 $k$ points in the whole Brillouin-zone. A similar density of $k$ points was used for the other structures. All calculations are performed with a 500-eV plane-wave cutoff. In order to avoid ambiguities regarding the total-energy results we have always used the same energy cutoff and a similar $k$-grid density for convergence for all structural variants tested. The present type of theoretical approach has recently been successfully applied to reproduce experimentally observed ambient- and high-pressure phases of metal hydrides.

For our theoretical simulation, 21 closely related potential structure types have been considered. The involved structure types are Li$_3$AlF$_6$, B$_2$BO$_6$, Na$_3$AlH$_6$, Na$_3$AlF$_6$, Na$_3$CrCl$_6$, Mg$_3$TeO$_6$, K$_3$MoF$_6$, K$_3$TiF$_6$, Fe$_3$BO$_6$, Cu$_3$TeO$_6$, Cu$_3$WO$_6$, Rb$_3$TiF$_6$, Nb$_3$BaO$_6$, Nb$_3$VS$_6$, I$_3$AsF$_6$, H$_3$SO$_4$.
The calculated total energy vs cell-volume curves for the 14 most relevant structural arrangements are shown in Fig. 1. Among them the Mg$_3$TeO$_6$-type arrangement (designated α-Li$_3$AlH$_6$; see Fig. 2). The pressure induced structural transition points are shown on the right-hand side of the illustration. Arrows mark the crossover points in the total-energy curves. The calculated total-energy curves vs cell-volume for Li$_3$AlH$_6$ in possible transition arrangements. Magnified versions around the structural transition points are shown on the right-hand side of the figure. Arrows mark the crossover points in the total-energy curves between the phases. Transition pressures are calculated from the Gibbs free-energy curves.

The calculated total energy vs cell-volume curves for the 14 most relevant structural arrangements (the others fall at higher total energy) are shown in Fig. 1. Among them the Mg$_3$TeO$_6$-type arrangement (designated α-Li$_3$AlH$_6$; see Fig. 2). The pressure induced structural transition points are shown on the right-hand side of the illustration. Arrows mark the crossover points in the total-energy curves. The calculated total-energy curves vs cell-volume for Li$_3$AlH$_6$ in possible transition arrangements. Magnified versions around the structural transition points are shown on the right-hand side of the figure. Arrows mark the crossover points in the total-energy curves between the phases. Transition pressures are calculated from the Gibbs free-energy curves.

FIG. 1. Calculated total energy vs cell volume for Li$_3$AlH$_6$ in possible structural arrangements. Magnified versions around the structural transition points are shown on the right-hand side of the illustration. Arrows mark the crossover points in the total-energy curves between the phases. Transition pressures are calculated from the Gibbs free-energy curves.

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1 and Table I) is found to have the lowest total energy, which is consistent with the recent experimental findings. The calculated unit-cell dimensions and positional parameters at 0 K and ambient pressure are in good agreement with room-temperature experimental findings [the calculated α is within 0.3% of the experimental value whereas the larger underestimate (0.6%) in the c direction is typical for the agreement obtained by density-functional calculations]. It is interesting to note that the β (Cu$_2$TeO$_6$-type) and γ (Li$_3$AlF$_6$-type) modifications are energetically very close to α-Li$_3$AlH$_6$. This indicates that synthesis under appropriate pressure and temperature conditions may be able to stabilize the β and γ modifications as metastable phases.

α-Li$_3$AlH$_6$ structure consists of isolated [AlH$_4$]$^-$ octahedra. Each Li atom is connected to two corners and two edges of these [AlH$_4$]$^-$ octahedra. There are two crystallographically different Al sites, both with equal Al-H distances within each octahedron, but with slightly deviating angles from the ideal 90° value. Al has eight nearest Al neighbors, in a cubic arrangement, and six more distanced neighbors placed about the faces of the cube.

In general, application of pressure will reduce the interatomic distances in a crystal structure and when the pressure exceeds a critical value a change in crystal structure occurs. The change in the structure brings about a change in the physical and chemical properties. As a result, application of pressure transforms α-Li$_3$AlH$_6$ into the β modification (with Cu$_2$TeO$_6$-type structure) at 18.64 GPa [the transition pressures are estimated from the pressure vs difference in Gibbs free-energy (ΔG) curves; see Fig. 2]. The pressure induced

<table>
<thead>
<tr>
<th>Modification (structure type)</th>
<th>Unit cell dimension (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Li$_3$AlH$_6$ (α)</td>
<td>$a = 8.0487 (8.0712)^a$</td>
<td>Li: 0.9334, 0.2196, 0.2804 (0.9576, 0.2260, 0.2911)$^a$;</td>
<td>35.75</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>$c = 9.4532 (9.513)^a$</td>
<td>Al(i1): 0.0, 0; Al(i2): 0.0, 0.1/2;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(i1): 0.8307, 0.8264, 0.0986 (0.8333, 0.8057, 0.1007)$^a$;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(i2): 0.1372, 0.2014, 0.3978 (0.1582, 0.1820, 0.3900)$^a$;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Li$_3$AlH$_6$ (Cu$_2$TeO$_6$; α5)</td>
<td>$a = 8.8532$</td>
<td>Li: 0.9596, 0.14; Al: 1/4, 1/4, 1/4;</td>
<td>36.09</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H: 0.3703, 0.1788, 0.3949</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Li$_3$AlH$_6$ (K$_2$TiF$_6$; Fd5)</td>
<td>$a = 13.9015$</td>
<td>Li(i1): 1/8, 1/8, 1/8; Li(i2): 5/8, 5/8, 5/8;</td>
<td>37.63</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li(i3): 1/4, 1/4, 1/4; Li(i4): 3/8, 1/8, 1/8;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al(i1): 0.0, 0; Al(i2): 1/2, 1/2, 1/2;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(i1): 0.1125, 0.0634, 0.0113;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(i2): 0.6124, 0.5634, 0.5101</td>
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<tr>
<td>δ-Li$_3$AlH$_6$ (Li$_3$AlF$_6$; Pna2$_1$)</td>
<td>$a = 9.2173$</td>
<td>Li(i1): 0.3798, 0.3697, 0.4991;</td>
<td>35.84</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>$b = 7.9755$</td>
<td>Li(i2): 0.1033, 0.4445, 0.5016;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 4.7258$</td>
<td>Li(i3): 0.3423, 0.5601, 0.004; Al: 0.1285, 0.2436, 0;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(i1): 0.2281, 0.0728, 0.1329;</td>
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<tr>
<td></td>
<td></td>
<td>H(i2): 0.0303, 0.2387, 0.3139;</td>
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<td>H(i3): 0.2333, 0.2487, 0.6940;</td>
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<td>H(i4): 0.2413, 0.3869, 0.1788;</td>
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<td>H(i5): 0.0198, 0.0855, 0.8283;</td>
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<td></td>
<td>H(i6): 0.0213, 0.3997, 0.8514</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$Experimental value from Ref. 14.
\( \alpha \)-to-\( \beta \) transition of LiAlH\(_4\) (see Figs. 1 and 2) involves reconstructive rearrangements (viz., bonds are broken and reestablished) of the cation and anion sublattices. \( \beta \)-LiAlH\(_4\) is stable in a fairly narrow pressure range and converts to \( \gamma \)-LiAlH\(_4\) (\( K_2\)TiF\(_6\)-type) at 28.85 GPa and further to \( \delta \)-LiAlH\(_4\) (\( Li_2AlF_6\)-type) at 68.79 GPa. \( \alpha \)-, \( \beta \)-, and \( \delta \)-LiAlH\(_4\) have very similar equilibrium volumes (87.76, 86.74, and 86.78 Å\(^3\)/f.u., respectively) and the energy difference between them is also very small (see Fig. 1). This closeness in total energy suggests that the relative appearance of these modification will be quite sensitive to, and easily affected by, external factors such as temperature and remnant lattice stresses. Another important point is that at the \( \alpha \)-to-\( \beta \) phase-transition point, the estimated volume difference is also small (Fig. 2) suggesting that \( \alpha \)-LiAlH\(_4\) has an efficiently packed structure. Similar is the process for the \( \beta \)-to-\( \gamma \) and \( \gamma \)-to-\( \delta \) transitions (Fig. 2). For comparison it may be recapitulated that the volume discontinuity at the \( \alpha \)-to-\( \beta \) transition point in LiAlH\(_4\) (Ref. 23) is \( \sim 17\% \). The closeness in volume of the different LiAlH\(_4\) modifications at the transition pressure should be a challenging task also for experimentalists.

The calculated bulk modulus \( B_0 \) and its pressure derivative \( B'_0 \), for different LiAlH\(_4\) phases are given in Table I. The involved phases have almost similar bulk moduli, which is partially due to the closeness in the equilibrium volumes of the different modifications. The estimated \( B_0 \) for LiAlH\(_4\) in the different modifications are closer to \( \beta \)-LiAlH\(_4\) than \( \alpha \)-LiAlH\(_4\). This indicates that LiAlH\(_4\) is harder than \( \alpha \)-LiAlH\(_4\) with strong bonding interactions between the constituents, which, in turn, may be the reason for the higher decomposition temperature of LiAlH\(_4\) compared with \( \alpha \)-LiAlH\(_4\).

The calculated total and partial density of states (DOS) for \( \alpha \)-LiAlH\(_4\) are shown in Fig. 3. There is a finite energy gap between the valence and conduction bands in all modifications of LiAlH\(_4\) (not shown for \( \beta \)-, \( \gamma \)-, and \( \delta \)-LiAlH\(_4\)). Hence LiAlH\(_4\) must be classified as nonmetallic. The estimated band gap \( E_g \) is varying between \( \sim 2.72 \) and 4.12 eV, but no experimental values are available for comparison. The estimated \( E_g \) for \( \alpha \)-LiAlH\(_4\) is \( \sim 3.52 \) eV, which is almost \( \sim 1 \) eV smaller than that in \( \alpha \)-LiAlH\(_4\), but it should be recalled that theoretically derived band gaps in semiconductors and insulators may be underestimated by 20–50\% (Ref. 24) compared with experimental values. Earlier experience\(^\text{19}\) for this type of materials shows that GGA underestimates \( E_g \) by \( \sim 1.4 \) eV compared with experiments.\(^\text{25}\) If we assume a similar underestimation for \( \alpha \)-LiAlH\(_4\), this compound should have an experimental gap of 4.9 eV. The calculated valence-band width is increased from 7.5 eV (in the \( \alpha \) phase) to 12 eV (in the \( \delta \) phase), which is due to the reduction in the interatomic distance upon pressure.

The partial DOS for Li shows (Fig. 3) that the \( s \) and \( p \) states of \( \alpha \)-LiAlH\(_4\) are energetically degenerate in the whole energy range, while Al-\( s \) and Al-\( p \) states are well separated. The energetic degeneration of the Al-\( p \) and H-\( s \) states together with the spatially favorable constellation of Al and

\[ \text{FIG. 2. Calculated pressure vs cell-volume relation for LiAlH}_4. \]

\[ \text{FIG. 3. Calculated total and partial DOS for } \alpha \text{-LiAlH}_4. \]

The Fermi level is set at zero energy and marked by the vertical dotted line; \( s \) states are shaded.
H facilitates covalent bonding between Al and H, an inference that is further substantiated by the charge-density and electron localization function (ELF) analyses (Fig. 4). The charge-density distribution and ELF for AlH facilitate covalent bonding between Al and H, reflecting that the interaction between Al and H in AlH is weaker than that in AlH. This in turn is only natural when the coordination number is increased and the bond strength between the Al and H is decreased. A corresponding study on structural stability of sodium and potassium hexahydroluminates is in progress, and the findings will be presented in a forthcoming paper.

In conclusion, the calculated structural parameters for AlH are in good agreement with the experimental findings. It is found that the ground-state structure of AlH becomes unstable at higher pressure. The high-pressure modifications and equilibrium structures have almost similar equilibrium volumes, and the energy difference between the involved phases is also very small. The electronic structure shows that, in all modifications, AlH has nonmetallic character.

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30Inorganic Crystal Structure Database (Gmelin Institut, Karlsruhe, 2001).
Reply to "Comment on electronic structure and structural stability study of Li$_3$AlH$_6"$

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(Dated: November 25, 2004)

The nature of the bonding in Li$_3$AlH$_6$ has been re-examined with additional analyses using density-functional calculations. From partial density of states, charge-density distribution, charge transfer, electron-localization function, crystal orbital Hamilton population, and Mulliken population analyses it is concluded that the interaction between Li and AlH$_6$ in Li$_3$AlH$_6$ is ionic and not covalent. Based on charge-density distribution, electron-localization function, and density of states analyses we earlier suggested that the interaction between Al and H is largely of the covalent type. However, the additional analyses indicate that the interaction between Al and H in the AlH$_6$ structural sub-units is of a mixed covalent ionic (i.e., covalent) character.

The chemical bonding in materials becomes complicated to evaluate when the number of constituents increases. For ternary and quaternary systems it is harder to estimate the bonding character. When we consider hydrides, it is even more complicated than for other compounds, because of the small size of the hydrogen and the only one valence electron which give rise to different bonding character for hydrogen in different chemical environments (valence state $+1$ or $-1$ as well as covalent and metallic character). We have recently demonstrated these features in a series of metal hydrides. In our previous work on Li$_3$AlH$_6$, the main focus was on the structural phase stability and electronic structure, but we also characterized the chemical bonding between the constituents based on results obtained from partial density of states (PDOS), charge density, and electron-localization-function (ELF) analyses. From these considerations we concluded without ambiguity that the interaction between Li and the AlH$_6$ structural units is ionic. The energetic degeneration of Al- and H- states (from inspection of DOS), the finite charge-density distribution between Al and H, the polarized nature of ELF at the H site toward Al, and the spatially constellation of Al and H led us to conclude that covalent bonding prevails between Al and H in the AlH$_6$ unit. Moreover, the energetic difference between Al and H is only 0.7, which also should favor covalent-type interaction between them.

A recent paper by Singh on Li$_3$AlH$_6$ describes the bonding between H and Al as purely ionic. The arguments for this interpretation is based on DOS analysis and long-range Coulomb interactions according to calculations using the linearized-augmented plane-wave (LAPW) method. As more H- states are present in the valence band (VB) than in the conduction band (CB), Singh concluded that the interaction between Al and H must be ionic. Agarwala and Singh have also performed a similar type of analysis on Na$_3$AlH$_6$, where a similar conclusion was reached (viz., ionic interaction between H and Al). The calculated DOS for Li$_3$AlH$_6$ by Singh is in perfect agreement with our findings. Hence, there is no ambiguity between the different computational methods, whereas the interpretation/understanding of the results differs. It is commonly recognized that it is difficult to characterize the nature of chemical bonding (in particular for hydrides) from DOS and integrated charges inside spheres alone. We have recently shown that on using a combination of charge density, charge transfer and ELF distribution along with other information one should be able to characterize the quite complicated chemical bonding in hydrides. In order to make a firmer conclusion about the nature of the chemical bond in Li$_3$AlH$_6$ we need more data from different perspectives. Hence, we have made additional calculations using advanced density-functional tools.

Each and every theoretical tool has some additional flexibility/facilities to evaluate bonding behavior. We have therefore now used different density-functional tools to gather as much information as possible regarding the chemical bonding in Li$_3$AlH$_6$. The calculations are made for the theoretical equilibrium structure parameters specified for Li$_3$AlH$_6$ in Ref. 4, and for the compounds chosen for test cases we have used experimental structural parameters. The DOS, charge density, charge transfer, and ELF are evaluated from the Vienna ab initio simulation package (VASP) and the crystal orbital Hamiltonian population (COHP) is evaluated using the TRLMTO-IT package. The Mulliken population analyses have been made with the help of the CRYSTAL03 code in which we used 5-11G, 6-31G, 6-311G, 8-31G, and 8-311G basis sets for H, Li, Be, Mg, and Al, respectively.

The calculated partial DOS of Al and H in Li$_3$AlH$_6$ are shown in Fig. 1, illustrating the following three main features: (1) The VB and CB are separated by a band gap of $\sim 3.8$ eV confirming that this compound is an insulator. (2) The VB is split into two separate regions by a $\sim 1.3$ eV energy gap. The lowest lying band (at $-1.5$ to $-5.5$ eV) mainly originates from Al with finite contributions from H states. The second region from $-4.5$ to $-2.2$ eV comprises energetically degenerate H and Al- and P states which we focused on as a favorable situation for formation of covalent bonding in Ref. 4. The spherically symmetric nature of s orbitals together with the energetic degeneration of H and Al- and P states, suggest that there should be a high probability for formation of covalent-type bonding between these atoms. (3) The
very small contribution from H-s in the unoccupied states above the Fermi level ($E_F$) is explained with the help of COHP analysis. The COHP, which is the Hamiltonian population weighted DOS, is identical to the crystal orbital overlap population. Negative value of COHP indicates bonding character and a positive value of COHP points at anti-bonding character. The DOS and COHP are evaluated using different computer codes and that is the reason for the slight energy shift between the DOS and COHP curves in Fig. 1, but the overall features are the same. The calculated COHP for Al-H (Fig. 1; lower panel) shows that bonding states are present below $\sim-2.8$ eV and non-bonding states between $\sim-2.8$ eV and $E_F$. The COHP for Li-H shows bonding states between $\sim-2.8$ eV and $E_F$. The presence of both bonding and anti-bonding H-H states within the VB indicates that the H-s state are almost filled and this could explain why there are few H-s states in the CB.

If the chemical bending between Al and H is purely ionic one would expect that Al-p and H-s states should be energetically well separated.\textsuperscript{[9]} Further, in a purely ionic situation one should not expect the finite electron-density distribution between Al and H seen in Fig. 2a. Moreover the charge-density distribution should be spherically symmetric around the H site if the bending is purely ionic. Hence we came to our initial conclusion that the bonding between Al and H in Li$_3$AlH$_4$ is largely covalent. For strong covalent bending Singh\textsuperscript{[7]} points out that the H-character should be distributed between the three \(\sigma-p\) manifolds. As the H-s character is very small in the CB (Fig. 1, upper panel), Singh concluded that covalent contribution is negligible. However, in the first place one cannot judge the character of chemical bonding in complex materials based on DOS analyses alone (see, e.g., see Ref. 2). Owing to ionic-covalent interactions all H-s orbitals will be filled and therefore both bonding and antibonding states of the \(\sigma-p\) hybrid are within the VB, as evident from our COHP analysis (see, e.g., Fig. 1).

If the bonding interaction between all constituents in Li$_3$AlH$_4$ is purely ionic one would expect narrow band features and certainly not the broad DOS features found for Li$_3$AlH$_4$ (which indicate overlap interaction between the constituents, viz. also for the purely ionic case the distinct DOS manifold around $\sim-7$ eV with 2 electrons per formula unit are contributed by one constituent). However, considerable amounts of electrons (according to the integrated DOS 35% from Al, 40% from H, and the remaining 15% from Li) from both Al-s and H-s indicate a finite degree of covalent character. If Al is in the 3+ state, negligible amounts of electrons would be left at the Al site resulting in a very small contribution from it to the VB. In fact, the integrated DOS yielded $\sim0.78$ electrons at the Al site and shows that the bonding interaction is not purely ionic. The insulating behavior can be explained as follows: Within one Li$_3$AlH$_4$ unit, the 3 electrons from Li will fill 3 of the 6 half-filled H-s orbitals and the remaining 3 half-filled H-s orbitals form covalent interaction with the three electrons from Al, resulting in the complete filling of VB which gives the material insulating behavior.

In order to understand the details of the chemical bending in Li$_3$AlH$_4$, Singh\textsuperscript{[7]} performed a test calculation with the position of one Li in the unit cell exchanged with an H. Such an analysis is questionable because although Li and H have one s electron in the outermost shell the former always takes the 1+- valence state whereas the latter in the ionic case takes either 1+ or 1- depending on the chemical environment.

In order to gain further understanding of the nature of the bending we have calculated the charge density, charge transfer, and ELF for $\alpha$-Li$_3$AlH$_4$. The results are shown in Fig. 2, where we show only the relation between Al and H since there is no ambiguity with regard to the ionic interaction between Li$^{+}$ and AlH$_4^{-}$. The charge-density distribution and charge-transfer plot indicate that a finite number of electrons are present between Al and H, which means that there is a finite covalent type of interaction between Al and H within the AlH$_4$ unit. The charge-transfer plot (Fig. 2b) clearly indicates that charges are depleted from Al and Li. The depletion is not spherically symmetric at the Al site, which implies that the bending is ionic with an appreciable covalent-type interaction (di-rectional bending) between Al and H. The ELF is another useful tool to distinguish between different bonding situations in solids.\textsuperscript{[11,12]} The value of the ELF is limited to the range 0 to 1. A high value of ELF corresponds to a low Pauli kinetic energy, as is found for covalent bonds or ionic
electron pairs. The calculated ELF for Li$_3$AlH$_6$ in Fig. 2c shows that the H electrons are polarized toward the Al site. A similar character of the ELF is found for the molecules C$_2$H$_4$ and C$_2$H$_6$, where the interaction between C and H is commonly recognized as covalent.\textsuperscript{12} Hence, one must conclude that there is a directional bonding character between Al and H in Li$_3$AlH$_6$.

In order to make a quantitative conclusion it would be useful to be able to identify the amount of electrons on a particular atom and populations between atoms. Although there is no unique definition to identify how many electrons that are associated with an atom in a molecule or a sub-unit of a solid it has nevertheless proved useful in many cases to perform population analyses. Due to its simplicity the Mulliken\textsuperscript{15} population scheme has become the most familiar approach to count electrons associated with a given atom. However, also this method is more qualitative than quantitative, giving results that are sensitive to the atomic basis. Mulliken charges are reported in Table 1 for several H-based test materials using examples which may provide benchmarks for systems with well recognized chemical bonding. LiH is a nearly pure ionic compound and the calculated Mulliken charges reflect a nearly pure ionic picture with Li$^+$ and H$^-$. The overlap population between Li$^+$ and H$^-$ is also close to zero, as expected for an ionic compound. Similarly in MgH$_2$, BeH$_2$, and AlH$_3$ the bonding interaction is mainly ionic, but the degree of ionicity is reduced from MgH$_2$ to BeH$_2$ and further to AlH$_3$, viz. these compounds exhibit some covalent character as evidenced by the non-zero overlap population. For the CH$_4$ molecule the overlap population takes a value of 0.384 consistent with the well known covalent interaction for this molecule. The Mulliken effective charges for Li, Al, and H in LiAlH$_4$ and Li$_3$AlH$_6$ indicate that the interaction between the Li and AlH$_2$/AlH$_3$ is ionic (one electron transferred from Li to AlH$_2$/AlH$_3$). There is a finite overlap population between Al and H within the AlH$_2$/AlH$_3$ units which reflects a partly covalent character of the Al-H bond. However, the magnitude of the overlap population is smaller than for purely covalent compounds. Also, the partial charges (around two electrons transferred from Al to H) implies that there is significant ionic contribution to the Al-H bond. The calculated integrated COHP indicates that the covalent Al-H interaction in LiAlH$_4$ is stronger than that in Li$_3$AlH$_6$. Similarly, the calculated Mulliken effective charges and overlap population indicates that the covalent Al-H interaction is reduced when we move from LiAlH$_4$ to Li$_3$AlH$_6$.

As a conclusion we thus find that the bonding nature of the hydrides LiAlH$_4$ and Li$_3$AlH$_6$ does not exhibit a simple ionic or covalent character. In fact the bonding interaction in these compounds is quite complicated. The interaction between Li and AlH$_2$/AlH$_3$ is ionic and that between Al and H comprises both ionic and covalent character. We believe that similar type of bonding situation prevails in all similar hydrides, but the magnitude of the ionic/covalent mixture will exhibit considerable individual variation. Our study indicates that several analysis tools must be consulted in order to make more assured conclusions regarding the bonding nature of such materials.

The authors gratefully acknowledge the Research Council of Norway for financial support and for the

![Fig. 2](Color online) Calculated (a) valence-electron charge density, (b) charge transfer, and (c) ELF plot for Li$_3$AlH$_6$. The illustrations refer to the (001) plane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>MEC</th>
<th>Overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>Li</td>
<td>-1.28</td>
<td>-0.066 (LiH)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.29</td>
<td>0.284 (C-H)</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>Mg</td>
<td>-1.67</td>
<td>-0.040 (MgH)</td>
</tr>
<tr>
<td>BeH$_2$</td>
<td>Be</td>
<td>1.02</td>
<td>0.045 (Be-H)</td>
</tr>
<tr>
<td>AlH$_3$</td>
<td>Al</td>
<td>-1.22</td>
<td>-1.14 (AlH)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.74</td>
<td>0.091 (AlH)</td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>Li</td>
<td>1.02</td>
<td>0.171 (LiH)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>1.02</td>
<td>-0.21 (LiH)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.75</td>
<td>-0.75 (Li-H)</td>
</tr>
<tr>
<td>Li$_3$AlH$_6$</td>
<td>Li</td>
<td>1.02</td>
<td>0.155 (LiH)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>1.02</td>
<td>-0.25 (Li-H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.85</td>
<td>-0.15 (Li-H)</td>
</tr>
</tbody>
</table>
puter time at the Norwegian supercomputer facilities.

First Principles Investigations on Hydrides: \( M_3\text{AlH}_6 \) (\( M = \text{Na, K} \))

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(Dated: December 1, 2004)

The structural stability of \( \text{Na}_3\text{AlH}_6 \) and \( \text{K}_3\text{AlH}_6 \) has been systematically investigated using accurate density-functional total-energy calculations. The experimentally known crystal structure of \( \alpha-\text{Na}_3\text{AlH}_6 \) is reproduced and \( \alpha-\text{K}_3\text{AlH}_6 \) is predicted to be isostructural (\( \alpha-\text{Na}_3\text{AlF}_6 \) type; space group \( P2_1/n \)). This structure contains a pseudo face-centered cubic \( \text{Al} \) sublattice and each \( \text{Al} \) atom is surrounded by distorted octahedra of hydrogen atoms with the long octahedral axis tilted from the \([001]\) direction toward \( <111> \). We predict that the \( \alpha \) modifications will not be stable at higher pressures. On application of pressure to \( \text{Na}_3\text{AlH}_6 \), the \( \alpha \) phase transforms into a \( \text{Cs}_3\text{NdCl}_6 \)-type structure at 19.8 GPa. Similarly \( \alpha-\text{K}_3\text{AlH}_6 \) transforms into two high-pressure forms: (1) \( \alpha \) transforms to \( \beta \) with \( \text{Rb}_3\text{TiF}_6 \)-type structure at 53.4 GPa and (2) \( \beta \) transforms to \( \gamma \) with \( \text{U}_3\text{ScSe}_6 \)-type structure at 60.2 GPa.

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Alkali- and alkaline-earth-metal-based complex aluminium hydrides, \( \text{MAIH}_4 \) \((M = \text{Li, Na, K})\) and \( \text{Mg}((\text{AlH})_2)_2 \), are expected to have a potential as viable modes for storing hydrogen. These hydrides have been demonstrated to have higher hydrogen storage capacity at moderate temperatures and pressures and lower cost than conventional hydride systems based on intermetallic compounds. The decomposition of \( \text{MAIH}_4 \) follows corresponding two-step endothermic processes. The first step involves the decompositions products \( M_3\text{AlH}_6 \), \( \text{Al} \), and \( H_2 \), and the second step \( \text{MAH} \), \( \text{Al} \), and \( H_2 \). In order to obtain a better understanding of the hydrogen absorption/desorption of these systems, an essential piece of information is the crystal structure. However, as these compounds contain light elements, determination of the structures by X-ray or neutron diffraction is not trivial and for this reason structural information is very sparse. Owing to the favorable hydrogen weight content and the discovery of reversibility of hydrogen absorption/desorption with addition of some additives, the \( \text{MAIH}_4 \) phases have obtained special attention. The crystal structures of \( \text{LiAIH}_4 \) and \( \text{NaAIH}_4 \) have been well established by experimental and theoretical studies. The structure of \( \text{KAIH}_4 \) was first predicted1 by theoretical means and later also confirmed experimentally.2 Similarly, in the \( M_3\text{AlH}_6 \) series the crystal structures of \( \text{Li}_3\text{AlH}_6 \) and \( \text{Na}_3\text{AlH}_6 \) are well established, whereas the structure of \( \text{K}_3\text{AlH}_6 \) has remained unknown.

Recent experimental evidence shows that reversible hydrogen absorption/desorption proceeds smoothly in \( \text{KAIH}_4 \) without introduction of catalytic additives.3 \( \text{KAIH}_4 \) is thus different from \( \text{LiAIH}_4 \) and \( \text{NaAIH}_4 \), which have to be doped with a transition-metal catalyst to obtain absorption/desorption reversibility and kinetics. Hence, \( \text{KAIH}_4 \) and \( \text{K}_3\text{AlH}_6 \) now receive considerable attention among the \( M_3\text{AlH}_6 \) and \( M_4\text{AlH}_8 \) phases. So far only a very limited number of theoretical studies on complex hydrides has been reported. To the best of our knowledge only one theoretical attempt4 has been made so far to identify the crystal structure of \( \text{K}_3\text{AlH}_6 \) using a so-called simulated annealing procedure. However, this endeavour failed because the results did not converge. In a previous study on \( \text{Li}_3\text{AlH}_6 \) we found that the equilibrium structure is not stable at elevated pressures and three high-pressure forms were predicted.5 In this communication we report the crystal and electronic structures of \( M_3\text{AlH}_6 \) \((M = \text{Na, K})\) obtained by accurate density-functional calculations.

Total energies have been calculated by the projected augmented plane-wave (PAW) implementation of the Vienna ab initio simulation package (VASP).7 The generalized-gradient approximation (GGA)8 were used to obtain accurate exchange and correlation energies for a particular configuration of the ions which are relaxed toward equilibrium until the Hellmann-Feynman forces are less than \( 10^{-3}\)eV/Å. Brillouin zone integration are performed with a Gaussian broadening of 0.1 eV during all relaxations. For the \( \alpha-\text{Na}_3\text{AlF}_6 \)-type structure we used...
512 k points in the whole Brillouin zone. A similar density of k points were used for the other structures. All calculations are performed with 500 eV plane-wave cutoff. In order to avoid ambiguities regarding the free-energy results we have used the same energy cutoff and calculations are performed with 500 eV plane-wave cut-off.

Table I: Optimized equilibrium structural parameters, bulk modulus (\( B_0 \)) and pressure derivative of bulk modulus (\( B'_0 \)) for \( \alpha\)-Na\(_3\)AlH\(_6\) and \( \alpha\)-K\(_3\)AlH\(_6\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell (Å or °)</th>
<th>Positional parameters</th>
<th>( B_0 ) (GPa)</th>
<th>( B'_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha)-Na(_3)AlH(_6)</td>
<td>( \alpha)-Na(_3)AlH(_6), ( P_2_1/mb )</td>
<td>a = 5.3974 (5.362)</td>
<td>11.9</td>
<td>4.1</td>
</tr>
<tr>
<td>( \gamma)-Na(_3)AlH(_6)</td>
<td>( \gamma)-Na(_3)AlH(_6), ( P_n m )</td>
<td>a = 4.8651</td>
<td>23.2</td>
<td>4.1</td>
</tr>
<tr>
<td>( \alpha)-K(_3)AlH(_6)</td>
<td>( \alpha)-K(_3)AlH(_6), ( P_2_1/mb )</td>
<td>a = 6.1771</td>
<td>16.0</td>
<td>0.2</td>
</tr>
<tr>
<td>( \beta)-K(_3)AlH(_6)</td>
<td>( \beta)-K(_3)AlH(_6), ( I_4/mmm )</td>
<td>c = 7.8098</td>
<td>24.6</td>
<td>4.1</td>
</tr>
<tr>
<td>( \kappa)-K(_3)AlH(_6)</td>
<td>( \kappa)-K(_3)AlH(_6), ( P_n m )</td>
<td>c = 2.5538</td>
<td>22.4</td>
<td>4.1</td>
</tr>
</tbody>
</table>

*Experimental value from Ref. 12.

The state-of-art approximation of density-functional theory. This means that one can reliably reproduce/predict the crystal structure of quite complex systems with this type of approach. Normally such theoretical simulations demand huge computer resources, but the development in the computer technology has made it possible to handle such systems (viz. structures with a considerable number of atoms per unit cell) within a reasonable time limit. Using a similar approach we have predicted structural parameters for the structurally uncharacterized K\(_3\)AlH\(_6\) compound. Calculated total energy versus cell volume curves for potential structures for K\(_3\)AlH\(_6\) are shown in Fig. 2. In order to have a good viewability among the 22 alternatives, we have displayed only the 11 types with the lowest total energy in Fig. 2. Among the considered structural arrangements for \( \alpha\)-K\(_3\)AlH\(_6\) the \( \alpha\)-Na\(_3\)AlF\(_6\) type is seen to possess the lowest total energy at 0 K and ambient pressure with unit-cell dimensions \( a = 6.1771, b = 5.8881, c = 8.6431 \AA, \) and \( \beta = 89.30^\circ \). The calculated formation energy for KAlH\(_4\) and \( \alpha\)-K\(_3\)AlH\(_6\) (\( \Delta H = -128.01 \text{ and } -224.69 \text{ kJ/mol} \), respectively) shows that both phases are stable.

Total-energy calculations show that \( \alpha\)-Na\(_3\)AlH\(_6\) in the \( \alpha\)-Na\(_3\)AlF\(_6\) and \( \beta\)-Na\(_3\)AlF\(_6\) structures are close in energy at the equilibrium volume, and the involved energy difference between the two variants is only \( \sim 0.13 \text{ eV/\text{f.u.}} \). This indicates that the competition between these structural arrangements will be sensitive to the
synthesis and examination temperature. The positional parameters for K$_3$AlH$_6$ in the α- and β-Na$_3$AlF$_6$-type structures are closely related except that the higher orthorhombic symmetry has enforced alignment of the [AlH$_6$]$^{10-}$ octahedra which take low index directions in the β-Na$_3$AlF$_6$-type arrangement.

The atomic arrangement of α-K$_3$AlH$_6$ is shown in Fig. 1. This structure consists of isolated [AlH$_6$]$^{10-}$ octahedra with the Al atoms arranged in a pseudo-face-centered cubic sublattice. Within the distorted octahedra the hydrogen atoms along the long octahedral axis are tilted from the [001] direction toward <111>. The other apices of the octahedra are oriented toward the corners of the unit cell and these four nearly equatorial H atoms are aligned to form a hydrogen superlattice in the [001] direction. Within the [AlH$_6$]$^{10-}$ units of α-K$_3$AlH$_6$ the Al-H bond lengths range from 1.76 to 1.81 Å, closely corresponding to the interatomic Al-H distances in α-Na$_3$AlH$_6$ (1.75–1.77 Å). The calculated H-Al-H bond angles within the [AlH$_6$]$^{10-}$ octahedra vary from 83.09 to 107.37°.

On application of pressure, α-Na$_3$AlH$_6$ transforms to the Cs$_5$NdCl$_6$-type γ phase at 19.8 GPa. A β modification has been identified by Bastide et al.\textsuperscript{13} at elevated temperature. However, the calculated total energy for this phase has almost 0.24 eV higher energy than α-Na$_3$AlH$_6$. The equilibrium volume for the α and γ modifications are almost the same (113.1 and 112.6 Å$^3$/f.u., respectively), but the involved energy difference is large (∼0.09 eV/f.u.). The calculated volume difference between the involved structures at the pressure-induced transition point is ∼4.5%. The high-pressure γ phase is stable at pressures above 19.8 GPa, the transition pressure being evaluated from the crossover point in the Gibbs free energy curves between α- and γ-Na$_3$AlH$_6$ (Fig. 3a).

α-K$_3$AlH$_6$ is stable up to 53.4 GPa where it transforms into a Rb$_3$TlF$_6$-type β modification (see Figs. 2 and 3b). In this pressure range the α-Na$_3$AlF$_6$, β-Na$_3$AlF$_6$, and Rb$_3$TlF$_6$ structure types are close in energy (within less than 10 meV). At higher pressures (around 60.2 GPa) the β modification transforms into a γ modification with U$_3$ScS$_6$-type structure. However, also the involved energy differences between these phases and the other closely related structural arrangements are very small. Our calculations have not included temperature effects, and at higher pressures one can expect multi-phase or superstructure formation or any one of the above mentioned higher-temperature variants in single-phase form depending on the experimental conditions. The calculated density of states for the equilibrium structures (α modifications) of Na$_3$AlH$_6$ and K$_3$AlH$_6$ shows that the conduction and valence bands are separated by almost 3.0 eV, and these materials must accordingly be classified as non-metals. It is interesting to note that another member of the series, Li$_3$AlH$_6$, has almost the same sized band gap (3.5 eV) although this compound stabilizes with a rather different structure.\textsuperscript{5}

In conclusion, the calculated structural parameters for α-Na$_3$AlH$_6$ are in excellent agreement with the experimental findings. The crystal structure of α-K$_3$AlH$_6$ is predicted. α-Na$_3$AlH$_6$ and α-K$_3$AlH$_6$ stabilize in the α-Na$_3$AlF$_6$-type structure. We found that the ground-state structure of these $M_3$AlH$_6$ phases becomes unstable at higher pressures. The high-pressure modifications and equilibrium structures have almost similar equilibrium volumes and the energy difference between the involved phases is very small for K$_3$AlH$_6$. The electronic structures show that all the equilibrium and high-pressure modifications of these compounds have non-metallic character.

The authors gratefully acknowledge the Research Council of Norway for financial support and for computer time at the Norwegian supercomputer facilities.

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\textsuperscript{4} S.C. Chung and H. Moroisa, J. Alloys Compd. 372, 92

FIG. 2. Calculated total energy versus cell volume curve for K$_3$AlH$_6$ in different possible structural arrangements (structure types stated on the illustration). Arrows indicate the crossover points in the total energy curves. Magnified versions around the structural transition points are shown on the right-hand side of the illustration. The transition pressures are calculated from the Gibbs free energy curves.

\textsuperscript{5} H. Fjellvåg, (unpublished)
FIG. 3: Stability of the high-pressure $\beta/\gamma$ phases of (a) Na$_3$AlH$_6$ and (b) K$_3$AlH$_6$ with respect to their equilibrium phases, transition pressures being marked by arrows at the corresponding transition points.

(2004).
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Theoretical Modeling of Hydrogen Storage Materials: Prediction of Structure, Chemical Bond Character, and High Pressure Behavior

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Abstract

Density-functional theory (DFT) is a powerful tool to predict crystal structure, chemical bond character, and high pressure behavior of materials. In this report we show the application of DFT to study such properties for complex hydrides. The structural parameters for the experimentally known Li₃AlH₆ phase have been successfully reproduced within an accuracy of less than 1% and the crystal structure of KAlH₄ has been predicted. From examination of the density of state we find that these materials have insulating behavior with band gap of ∼3.5 and 5.5 eV for Li₃AlH₆ and KAlH₄ respectively. From analyses of charge density, charge transfer, electron localization function, crystal orbital Hamilton, and Mulliken population we find that the interaction between Li/K and [AlH₄]/[AlH₆] is purely ionic, whereas within the [AlH₄]/[AlH₆] unit the interaction is partially ionic and partially covalent. Even though these materials are very soft the Al–H interaction is relatively strong compared with the other interactions. Subject to external pressure the equilibrium structure of Li₃AlH₆ is unstable. We predicted that this compound undergoes three successive structural phase transitions under pressure: α to β at 18.64 GPa, β to γ at 28.85 GPa, and γ to ε at 68.79 GPa. KAlH₄ is stable and no pressure induced structural transitions were identified.

Key words: Complex hydrides; Theoretical modeling; Structural stability; Chemical bond character; High-pressure behaviour.
1 Introduction

High capacity solid-state storage of hydrogen is becoming increasingly important for fuel-cell power plants and automotive and electrical utility applications. One of the major drawbacks of known reversible metal hydrides applicable for hydrogen storage in comparison to liquid hydrogen is their low gravimetric hydrogen content (expressed in wt.% of H in the material): MgH$_2$, 7.6 wt% H and hydrides of Mg alloys (e.g., Mg$_2$NiH$_4$, 3.8 wt.% H) represent in this respect the current optimum. However, for their use as storage materials a sufficient amount of heat ca. 300°C is necessary for the desorption of the hydrogen. The disadvantage of the presently known, low- and medium-temperature reversible hydrides are the high costs for the intermetallic alloys suitable for the purpose (LaNi$_5$H$_6$, TiFeH$_2$), combined with their 4–5 times lower storage capacity (1.8 wt.% H) compared with say MgH$_2$.

Alkali metal-based aluminum hydrides, $AAIH_4$ ($A =$ Li, Na, K) have been found to have a potential as viable modes for storing hydrogen at moderate temperatures and pressures. These hydrides have been demonstrated to have higher hydrogen storage capacity at moderate temperatures and lower cost than conventional inter-metallic hydrides. However, a serious problem with these materials is poor kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Bogdanovic and co-workers [1,2] have recently established that sodium aluminum hydrides, which were earlier considered in actual practice as irreversible with respect to hydrogen absorption/desorption, can be made reversible by doping with Ti. Efforts [3,4] have also been made to improve the hydrogen reversibility of NaAlH$_4$ by ball milling in combination with or without additives. In line with this, considerable interest is attached to the structural properties of the series $ABH_4$ and $A_3BH_6$ ($A =$ alkali metal, $B =$ B, Al, Ga) at ambient and higher pressures. In this article we will demonstrate how density-functional theory (DFT) is used to predict unknown crystal structures, chemical bond characteristics and high-pressure behaviour of hydrides.

In the first part of the paper we present the structural calculations for of some complex hydrides. In the second part we will consider the chemical bonding in selected hydrides with the help of partial density of states (DOS), crystal-orbital Hamilton population (COHP), charge density, charge difference, and electron-localization function (ELF). The third part deals with the structural stability of materials at high-pressures based on total-energy studies.
To predict the ground-state structure of Li$_3$AlH$_6$ and KAlH$_4$, we have used DFT [5] within the generalized-gradient approximation (GGA) [6], as implemented with a plane-wave basis in the Vienna *ab initio* simulations package (VASP) [7]. Results are obtained using projector-augmented plane wave (PAW) [8] potentials provided with the VASP. The atoms are relaxed toward equilibrium until the Hellmann–Feynman forces are less than $10^{-3}$ eV/Å. Brillouin zone integration are performed with a Gaussian broadening of 0.1 eV during all relaxations. All calculations are performed with 512 and 600 $k$ points for Li$_3$AlH$_6$ ($\alpha$-Li$_3$AlH$_6$) and KAlH$_4$ (KGaH$_4$-type structure), respectively, in the whole Brillouin zone with a 600 eV plane-wave cutoff. In order to avoid ambiguities regarding the free-energy results we have always used the same energy cutoff and a similar $k$-grid density for convergence for all structural variants tested. The present type of theoretical approach has recently been successfully applied [9–12] to reproduce structural properties of ambient- and high-pressure phases. The COHP is evaluated using the TBLMTO-47 package [13]. The Mulliken population analyses were made with the help of the CRYSTAL03 code in which we used 5-11G, 6-11G, 85-11G, 86-511G basis sets for H, Li, Al, and K, respectively [14].

### 3 Structural Prediction

Prediction and understanding of properties of materials (encompassing even not yet synthesized phases) by theoretical means is a valuable complement to the traditional experimental approach. Theoretical simulation of material properties before preparation and testing may save time, manpower, running costs etc. Owing to the low X-ray scattering power of hydrogen, poor crys-
Fig. 2. Structural competition between different possible modifications in Li$_3$AlH$_6$. Magnified versions around structural transition points are shown on the right-hand side of the illustration. Arrows mark the crossover points in the total-energy curves between the phases. Transition pressures are calculated from the Gibbs free-energy curves.

tallinity, and the usual structural complexity of hydrides, these structures are often less characterized than other solids. For instance, this is the case for the (assumed technologically interesting materials) alkali boron, alkali aluminum and alkali gallium tetrahydrides among which only few are structurally well characterized. In this present section we are going to show how DFT calculations can be used to predict the structures of experimentally structure characterized Li$_3$AlH$_6$ (Fig.1) and uncharacterized KAlH$_4$ compounds.

3.1 The crystal structure of Li$_3$AlH$_6$

The crystal structure of Li$_3$AlH$_6$ has up to recently not been completely revealed and several structure models have been proposed with possible monoclinic (P2$_1$/c, P2$_1$/m, C2/m or C2) and rhombohedral (R3, R3, R3m or R3$\bar{m}$) space groups [15–17]. There has been no theoretical attempt to explore the crystal and electronic structures of this compound. However, a fresh experimental study by Brinks and Hauback [18] with combined synchrotron X-ray and neutron diffraction has shown that Li$_3$AlH$_6$ crystallizes in space group R3.
Twenty one closely related potential structure types were considered for the theoretical simulation. The involved structure types are: Li$_3$AlF$_6$, B$_3$BO$_6$, Na$_3$AlH$_6$, Na$_3$AlF$_6$, Na$_3$CrF$_6$, Mg$_3$TeO$_6$, K$_3$MoF$_6$, K$_3$TIF$_6$, Fe$_3$BO$_6$, Cu$_3$TeO$_6$, Cu$_3$WO$_6$, Rb$_3$TeF$_6$, Nb$_3$BaO$_6$, Nb$_3$VS$_6$, I$_3$AsF$_6$, Hg$_3$SO$_6$, Hg$_3$NbF$_6$, Hg$_3$TeO$_6$, Pb$_3$SO$_6$, Er$_3$GaS$_6$, and U$_3$SeS$_6$ [19]. The calculated total energy versus cell-volume curves for the 14 most relevant structural arrangements (the others fall at higher total energy) are shown in Fig. 2. Among them the Mg$_3$TeO$_6$-type arrangement (designated α-Li$_3$AlH$_6$; Fig. 2 and Table 1) is found to have the lowest total energy, consistent with the recent experimental findings [18]. The calculated unit-cell dimensions and positional parameters at 0 K and ambient pressure are in good agreement with the room temperature experimental findings [the calculated $a$ is within 0.3% of the experimental value whereas the slight underestimation (0.6%) in the $c$ direction is typical for the agreement obtained by DFT calculations]. It is interesting to note that the β (Cu$_3$TeO$_6$ type) and γ (Li$_3$AlF$_6$ type) modifications are energetically very close to α-Li$_3$AlH$_6$. This indicates that synthesis under appropriate pressure and temperature conditions may be able to stabilize the β and γ modifications as meta-stable phases.

The α-Li$_3$AlH$_6$ structure consists of isolated [AlH$_6$]$_3^-$ octahedra. Each Li atom is connected to two corners and two edges of these [AlH$_6$]$_3^-$ octahedra. There are two crystallographically different Al sites, both with equal Al−H distances within each octahedron, but with slightly deviating angles from the ideal 90° value. Al has eight nearest Al neighbors, in a cubic arrangement, and six more distanced neighbors placed about the faces of the cube.

### Table 1
Optimized structural parameters for Li$_3$AlH$_6$ and KAlH$_4$.

<table>
<thead>
<tr>
<th>Compound (structure type, space group)</th>
<th>Unit-cell dimension (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Li$_3$AlH$_6$ (Mg$_3$TeO$_6$, R3)</td>
<td>$a = 8.9487$ (8.9712)$^a$</td>
<td>Li(18f) : 0.9334, 0.2196, 0.2804 (0.9576, 0.2260, 0.2911)$^b$; Al1(3a) : 0.0, 0.0, 0.0, Al2(3b) : 0.0, 0.0, 1/2; H1(18f) : 0.8307, 0.8264, 0.0986 (0.8333, 0.8057, 0.1007)$^b$; H2(18f) : 0.1372, 0.2014, 0.3978 (0.1582, 0.1820, 0.3900)$^b$</td>
<td>35.75</td>
</tr>
<tr>
<td>KAlH$_4$ (KGaH$_4$, Pnma)</td>
<td>$a = 8.8249$ (8.8440)$^b$</td>
<td>K (4c) : 0.1778, 1/4, 0.1621</td>
<td>10.34</td>
</tr>
<tr>
<td></td>
<td>$b = 5.8590$ (5.8190)$^b$</td>
<td>Al (4c) : 0.5663, 1/4, 0.8184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 7.3872$ (7.3310)$^b$</td>
<td>H1 (4f) : 0.4034, 1/4, 0.9184</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2 (4c) : 0.7055, 1/4, 0.9623</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>H3 (6d) : 0.4194, 0.9810, 0.3127</td>
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</table>

$^a$Experimental value from Ref. [18].
$^b$From XRD measurements [20].
3.2 Crystal structure of KAlH₄

Recent experimental evidence shows that reversible hydrogen absorption/desorption proceeds smoothly in KAlH₄ without introduction of a catalyst [21]. KAlH₄ is thus different from LiAlH₄ and NaAlH₄, which have to be doped with a transition metal catalyst to obtain absorption/desorption irreversibility and kinetics. Hence, KAlH₄ has now received considerable attention among the alkali-metal aluminum hydrides. The crystal structures of LiAlH₄ and NaAlH₄ are well known, whereas a more complete structural description for KAlH₄ has not yet been reported. The present structural knowledge being limited to unit-cell dimensions at room temperature [20].

Among the seven tested possible structural variants (structure types specified in Refs. [9,11,22]), the orthorhombic KGaH₄-type arrangement (Table 1) is seen to have the lowest total energy with unit-cell dimensions a = 8.324, b = 5.559, c = 7.357 Å at 0 K and ambient pressure. However, the tetragonal α-NaAlH₄-type phase is energetically very close to the KGaH₄-type ground-state phase. This indicates that syntheses under appropriate pressure and temperature conditions may be able to stabilize the α-NaAlH₄-type arrangement as
a metastable state. The KGaH$_4$- and α-NaAlH$_4$-type variants of KAlH$_4$ have not only a small total-energy difference, but their equilibrium volumes are similar ($V_0 = 96.15$, and 93.95 Å$^3$/f.u., respectively). The calculated cell volume for the KGaH$_4$-type ground-state variant is in very good agreement with the observations, remembering that the calculations refer to 0 K and the experimental values to room temperature. A recent powder neutron diffraction study [23] on KAlH$_4$ confirms our predictions and the calculated positional parameters are in good agreement.

KAlH$_4$ is isostructural and isoelectronic with KGaH$_4$ whereas other isoelectronic compounds like NaAlH$_4$ and NaGaH$_4$ take rather different crystal structures. The KAlH$_4$ ground-state structure consists of slightly distorted [AlH$_4$]$^-$ tetrahedra which are separated by intermittent K$^+$ cations. The interatomic Al–H distance within the [AlH$_4$]$^-$ tetrahedra varies only by 3% and the bond length is as expected for an anionic complex of Al and H [24]. Each K is surrounded by 12 H atoms at distances varying between 2.684 and 3.561 Å. The α-NaAlH$_4$-type structures of the proposed metastable modification of KAlH$_4$ also comprises tetrahedral [AlH$_4$]$^-$ anions and K$^+$ cations, but in a different mutual arrangement (see Fig.1a in Ref. [9]).

4 Chemical bonding

The chemical bonding in materials becomes complicated when the number of distinguishable constituent increases. For binary compounds one can easily assess the degree of ionic character from electronegativities using Gordy’s approximation [25]. For ternary and quaternary phases it is harder to estimate the ionic character. When we consider hydrides, it is even more complicated than for other compounds, because of the small size of hydrogen atom and its only one valence electron. It is important to understand the bonding character of materials in detail in order to explain why some materials have peculiar properties compared to other materials in say, a certain series. For example, the RNiInH$_{1.333}$ ($R =$ La, Ce, Pr, Nd) series of compounds violates the so-called “2Å - rule” for metal hydrides with the H–H separations of ≈1.6 Å [26]. The reason appears to be that the presence of strong interaction between the transition metal Ni and hydrogen in prohibits the electrons at the hydrogen atoms from participation in repulsive interaction between two closely arranged H atoms. Moreover, the $R$–$R$ interaction also shielding the repulsive interaction between the H atoms [27–29]. The bonding features of RNiInH$_{1.333}$ series have been explained with the help of partial density of states (PDOS), charge density distribution, charge difference plot, electron localization plot (ELF) and crystal orbital Hamiltonian population analysis (COHP) [27]. Our experience with this series of hydrides shows that several theoretical methods are needed in order to characterize the bonding correctly in order not to end up
with wrong conclusions [27–29].

In this present study we try to explore the bonding in KAlH$_4$ and Li$_3$AlH$_6$. We believe that a similar type of bonding may be present in the whole AMH$_4$ (A = Li, Na, K, Rb, Cs; M = B, Al, Ga), $A_3$AlH$_6$ ([A = Li, Na, K] family, because all these compounds have almost similar charge-density distribution, DOS, and ELF. The calculated DOS of KAlH$_4$ and Li$_3$AlH$_6$ and partial DOS of KAlH$_4$ are displayed in Fig. 3. From the total DOS in the lower panel it is clear that KAlH$_4$ and Li$_3$AlH$_6$ are to be classified as insulators with a band gap of ca. 3.5 and 5.5 eV for Li$_3$AlH$_6$ and KAlH$_4$ respectively, which is close to the band gaps in other technologically interesting hydrides, viz. MgH$_2$ (4.3 eV [10]), LiAlH$_4$ (4.8 eV [11]), and NaAlH$_4$ (5.0 eV [9]). The PDOSs of KAlH$_4$ and Li$_3$AlH$_6$ show close similarities, hence we present only the DOS for KAlH$_4$. The site-projected DOSs of K and Al show that the lower peak in the total DOS mainly originates from Al-$s$ with small contribution from H-$s$, K-$s$, and K-$p$ states, whereas the upper peak has contributions from H-$s$, Al-$p$, K-$s$, and K-$p$ states. The Al-$s$ and Al-$p$ states are energetically well separated in the valence band (VB) whereas the K-$s$ and -$p$ states are energetically degenerated throughout the VB. Al-$p$ and H-$s$ states are energetically degenerated in corresponding energy regions in the VB which is a favorable situation for formation of covalent bonds within the anionic [AlH$_4$]$^-$ complex. From an electronegativity point of view, the bonding Al—H interaction is also expected to be of a covalent nature, whereas the K—H, Li—H interaction should be ionic.

Fig. 4 shows the calculated valence-charge density of KAlH$_4$. At the K, Al, and H sites, it is clear that the highest amount of charge density resides in the immediate vicinity of the nuclei. There is a finite electron distribution between Al and H which is another indication for covalent type of interaction. However, the electron distribution between K and the [AlH$_4$] unit is almost zero (charge depleted; see Fig. 4 b), viz. an indication for ionic type of interaction between K and [AlH$_4$]. The calculated charge-transfer plot (charge-density difference between the solid and overlapping free atomic orbitals) clearly show that charges are depleted from the K and Al sites and transferred to the H sites, viz the interaction between the K/Al and H is partial ionic. For a purely ionic case
Table 2
Mulliken population analysis for Li$_3$AlH$_6$ and KAlH$_4$. Mulliken effective charge (difference between the number of electrons and Mulliken charge; MEC) and overlap population in units of e.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>MEC</th>
<th>Overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$AlH$_6$</td>
<td>Li</td>
<td>$-1.008$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>$-2.032$</td>
<td>$-0.014$ (Li–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$+0.844$</td>
<td>$0.105$ (Al–H)</td>
</tr>
<tr>
<td>KAlH$_4$</td>
<td>K</td>
<td>$-1.098$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>$-1.880$</td>
<td>$-0.015$ (K–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$+0.749$</td>
<td>$0.171$ (Al–H)</td>
</tr>
</tbody>
</table>

one can expect a perfect spherically symmetric charge depletion as observed at the K site. But the charge depletion at the Al site is not spherically symmetric in the two systems under consideration. Similarly the calculated ELF at the H sites is not spherically symmetric indicating that the electrons are polarized toward the Al site (Fig. 4 c). A similar type of ELF is found in molecular C$_2$H$_6$ and C$_2$H$_4$, where the interaction between C and H is covalent [30]. Hence, one can expect directional bonding in-between Al and H in KAlH$_4$ and Li$_3$AlH$_6$. The calculated integrated COHP values indicates that the interaction between Al and H is the strongest (ICOHP value $-2.39$ eV) compared to other interactions and the estimated bond strength vary in the sequence Al–H K/Li–H K/Li–Al H–H. In order to have some quantitative picture of the charge-transfer effect we also made the Mulliken population analyses [31]. The Mulliken effective charges for Li, K, Al, and H in Li$_3$AlH$_6$ and KAlH$_4$ indicate (see Table 2) that the interaction between Li/K and [AlH$_6$] or [AlH$_4$] is purely ionic; viz, approximately one electron is transferred from Li or K to [AlH$_6$] or [AlH$_4$]. There is a finite overlap population present between Al and H within the [AlH$_6$]/[AlH$_4$] units. This arises due to the partial covalent nature of the Al–H chemical bond. However, the magnitude is smaller than that in purely covalent compounds and the partial charges (around two electrons transferred from Al to H) implying a finite degree of ionic interaction.

5 Pressure induced structural transition

In general, application of pressure will shorten the interatomic distances in a crystalline solid and when the pressure exceeds a critical value a change in crystal structure occurs. The change in the structure brings about a change in the physical and chemical properties. In some cases the high-pressure phases have peculiar properties compared with ambient-pressure phases. For example in LiAlH$_4$ we note a huge pressure induced volume collapse (around 17%) at the $\alpha$ to $\beta$ transition point [11]. Similarly in BeH$_2$ there is an almost 26.4% reduction in volume at the phase transition point from the equilibrium to a
Application of pressure transforms $\alpha$-Li$_3$AlH$_6$ into the $\beta$ modification (with Cu$_3$TeO$_6$-type structure) at 18.64 GPa (transition pressures are estimated from the pressure vs. difference in Gibbs free energy ($\Delta G$) curves; see Fig. 5). The pressure induced $\alpha$-to-$\beta$ transition of Li$_3$AlH$_6$ (see Figs. 2 and 5) involves reconstructive rearrangements (viz. bonds are broken and re-established) of atomic architecture. $\beta$-Li$_3$AlH$_6$ is stable in a fairly narrow pressure range and transform into $\gamma$-Li$_3$AlH$_6$ (K$_3$TIF$_6$ type) at 28.85 GPa and further to $\delta$-Li$_3$AlH$_6$ (Li$_3$AlF$_6$ type) at 68.79 GPa. $\alpha$-, $\beta$-, and $\delta$-Li$_3$AlH$_6$ have very similar equilibrium volumes (87.76, 86.74, and 86.78 Å$^3$/f.u., respectively) and the energy difference between them is also very small (see Fig. 2). This closeness in total energy suggests that the relative appearance of these modifications will be quite sensitive to, and easily affected by, external factors like temperature and remnant lattice stresses. Another important point is that at the $\alpha$-to-$\beta$ phase-transition point, the estimated volume difference is also small (Fig. 5) suggesting that $\alpha$-Li$_3$AlH$_6$ has an efficiently packed structure; similarly for the $\beta$-to-$\gamma$ and $\gamma$-to-$\delta$ transitions (Fig. 5). As mentioned the volume discontinuity at the $\alpha$-to-$\beta$ transition point in LiAlH$_4$ [11] is $\sim$17%. The closeness in volume for the different Li$_3$AlH$_6$ modifications (at transition pressure) should challenge the experimentalists to study this system carefully.
The calculated bulk modulus $B_0$ for $\text{Li}_3\text{AlH}_6$ and $\text{KAlH}_4$ indicate that these materials are easily compressible solids. If we compare $B_0$ of diamond (432 GPa) with the studied phases (32 and 10 GPa for $\text{Li}_3\text{AlH}_6$ and $\text{KAlH}_4$, respectively) these compounds are having 13 to 43 times smaller $B_0$ values. Hence one may have expected that the removal of H from these structure should have been quite easy. This is certainly not the case. The COHP study on these materials [33] shows that the interaction between Al and H is stronger ($-2.62$ to $-3.44$ eV) than the other interactions, and this appears to a likely reason for these hydrides at the same time being very soft and yet require much energy to remove all hydrogen.

6 Conclusion

In this study we have sucessfully reproduced the structural properties of $\text{Li}_3\text{AlH}_6$ calculated positional and cell parameters being in very good agreement with experimental findings. We have predicted the crystal structure of $\text{KAlH}_4$. This ultimatively indicates that the density-functional theory is a powerful tool to predict structural properties of materials at ambient and high pressures. One can formally treat $\text{KAlH}_4$ as a pure ionic compound but the detailed analysis on this compound shows that whereas the interaction between the K and $[\text{AlH}_4]$ is ionic that between Al and H is mixture of ionic and covalent with the latter as the stronger component. This may be the possible reason why $\text{KAlH}_4$ (and $\text{Li}_3\text{AlH}_6$) has a high decomposition temperature. Due to close similarity in charge density and density of states distributions one can expect similar features in the whole $\text{AAlH}_4$ ($\text{A} = \text{Li, Na, K, Rb, Cs}$) family. From the high-pressure study on $\text{Li}_3\text{AlH}_6$ and $\text{KAlH}_4$, it is found that the ground-state structure of $\text{Li}_3\text{AlH}_6$ is not stable at higher pressure. Three high-pressure forms of $\text{Li}_3\text{AlH}_6$ have been identified. On the otherhand, $\text{KAlH}_4$ is a stable compound which exhibit no pressure induced transitions.

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