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Titanium and native defects in LiBH_4 and NaAlH_4

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Abstract

We report combined density functional studies and thermodynamic considerations on Ti-related and native defects in lithium borohydride and sodium alanate. Ti atoms introduced into the bulk of LiBH_4 are thermodynamically unfavorable for all their oxidation states, while high oxidation states of Ti^{n+} cations may become thermodynamically stable in the bulk of NaAlH_4 at certain thermodynamic conditions. Neutral hydrogen vacancies and interstitials or cation vacancies are less stable than their charged counterparts in both compounds. In sodium alanate, the formation of native defects leads to changes of the coordination number of aluminum, while in lithium borohydride BH_4 groups change their mutual orientation but B–H bonds remain intact. The electronic band alignment in LiBH_4 and NaAlH_4 is different.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Complex hydrides are interesting materials for mobile hydrogen storage [1, 2]. Among them sodium alanate (NaAlH_4) is a model system that is the most comprehensively studied, even though it does not fulfill expected gravimetric hydrogen storage density [3]. The lithium borohydride (LiBH_4), on the other hand, has much better hydrogen storage capacity, but at present it is considered as an irreversible storage medium (cannot be easily regenerated).

The activity of titanium for the improvement of the reversibility of hydrogen (re)adsorption on NaAlH_4 is well established [4, 5]. It is not clear if a similar catalytic effect can be achieved for LiBH_4 ; if so, then what a possible catalyst it could be. Recent research concerns studies of LiBH_4 modification via mixing with other hydrides (MgH_2), amides (LiNH_2) [6, 7] and metal additives [8]. It was recently shown that Ti enhances decomposition of LiBH_4 : unfortunately it does not facilitate synthesis of this compound [8]. No method that facilitates LiBH_4 as a practical hydrogen storage media is known.

The catalytic effect of metal additives on the kinetics of hydrogen adsorption/desorption is not understood on the microscopic level, even for sodium alanate. In particular, the basic question whether Ti penetrates inside the crystal

lattice and affects the stability of the bulk NaAlH_4 [9] or Ti activity is limited to the surface only [10] is still under debate. Several theoretical studies provide insight into the interaction mechanism of Ti atoms with NaAlH_4 [11–15]. Recent studies concerning the thermodynamic stability of mixed complex hydrides [16, 17] have proven that calculations may predict compositions of mixed complex hydrides that are less stable than each of their compounds separately [17]. While knowledge of the thermodynamic stability of various phases and compounds is necessary for analysis of new reactions and reaction paths it does not provide information on the atomic level. Processes on that level lead to decomposition (synthesis) of a compound. Thus the natural step towards an understanding of catalytic aspects of stabilization/destabilization of complex hydrides would include analysis of thermodynamic stability on the atomic level. The kinetics of (de)hydriding reactions is related to the mass transport and atomic/molecular diffusion, which on the atomic scale consist of a hopping motion of single atoms or molecules. The microscopic ground state and the knowledge about distribution and properties of point defects provide information on the thermodynamic driving force for atomic motion. The full picture shall include free energy barriers but this is not considered here.

In the present paper, we focus on thermodynamics of simple defects in LiBH_4 and NaAlH_4 . Such defects are related

to diffusion, and their thermodynamic stability defines the ground or intermediate states or the driving force for atomic motion. We provide evidence of very different behavior of Ti in LiBH₄ and NaAlH₄. Our studies also show a suitable methodology to study effects related to metal incorporation in complex hydrides. We show that incorporation of Ti into LiBH₄ is energetically unfavorable, while Ti cations at high oxidation states might be incorporated into the bulk of NaAlH₄ at certain thermodynamic conditions. These suggest that for lithium borohydride Ti has only the surface effect (thus facilitate decomposition), while in sodium alanate Ti may penetrate the bulk and interact with charged native defects. The neutral hydrogen vacancies or the interstitial are, in general, less stable than their charged counterparts in the bulk of both compounds. Our comparison also shows that additives forming anions might be stable in LiBH₄.

2. Methods

The present calculations are based on a periodic density functional (DFT) approach [18]. They concern energy and the electronic structure modification related to the formation of Ti defects (substitutions and interstitials) in the bulk and on the surface. Additionally we study the formation of the simplest intrinsic defects, like hydrogen, BH₄, AlH₄, Li, Na vacancies and H interstitials. Various oxidation states of Ti and all defects were considered.

The calculations were performed on supercells with 96 atoms for both compounds. The valence configurations 1s²2s¹ for Li, 2s²2p¹ for B, 2p⁶3s¹ for Na, 3s²3p¹ for Al, 3p⁶3d²4s² for Ti and 1s¹ for H were represented by projected augmented wave potentials [19]. The ground state electronic density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian. The spin polarized generalized gradient approximation (GGA) was used for the exchange–correlation functional [20]. An additional dense grid for the augmentation charges was applied. The charge state $n\pm$ of Ti or vacancies was obtained by addition of the uniform background charge to the supercell. More technical details are presented below along with a discussion of the accuracy of the present approach.

Surface calculations were performed for the lowest energy facets: the (001) surface of NaAlH₄ [15] and (100) for LiBH₄ [21]. The slab geometry with vacuum extending over 12 Å was used. Ti was interacting with one side of the slab, while the other was frozen. In the course of calculations the internal atomic positions were relaxed via the conjugate gradient method until the forces exerted on atoms were below 0.01 eV Å⁻¹. In several cases additional short simulated annealing runs were performed followed by relaxation of the atomic positions. The shape and volume of the unit cell was kept fixed at the equilibrium bulk dimensions.

The formation energy of Ti incorporated into the hydride lattice at the oxidation state $n\pm$ is defined as

$$\Delta E(\text{Ti}^{n\pm}) = E_{\text{tot}}(\text{Ti}^{n\pm}) - E_{\text{tot}}(\text{C.H.}) - \mu_{\text{Ti}} + \mu_{\text{A}} \pm n[\mu_{\text{e}} + \Delta V] \quad (1)$$

where μ_{A} stands for the chemical potential of Li, Na, Al or α -B. The solid metal state was taken as a reference for μ_{A} .

For interstitial Ti formally $\mu_{\text{A}} = 0$. C.H. stands for complex hydride, i.e. LiBH₄ or NaAlH₄, respectively. $E_{\text{tot}}(\text{Ti}^{n\pm})$ is the total energy derived from the supercell calculations with one substitution or interstitial at the charge state $n\pm$, while $E_{\text{tot}}(\text{C.H.})$ is the total energy of the equivalent neutral supercell with pure borohydride or alanate. The chemical potential of the electron reservoir is $\mu_{\text{e}} = E_{\text{F}} - E_{\text{v}}$, where E_{F} is the Fermi energy referenced to E_{v} —the valence band maximum. The origin is made such that $\mu_{\text{e}} = 0$ for $E_{\text{F}} = E_{\text{v}}$. ΔV is an alignment correction for the reference potential [22]. In binary metal oxides alignment of the electrostatic potential is usually done by comparison of some region far away from the defect. In the case of complex hydrides atomic relaxation involves rotation of the molecular units that carry charge. These can affect electrostatic potential in the vicinity of the rotated molecule and falsify alignment. To minimize such effects the electrostatic potential along the line between two metal cations that are far from defects was aligned. These cations were chosen for each defect separately such that there were no anionic groups along the line connecting them.

The formation energy of the vacancy is defined as

$$\Delta E(V_{\text{X}}^{n\pm}) = E_{\text{tot}}(V_{\text{X}}^{n\pm}) - E_{\text{tot}}(\text{C.H.}) + \mu_{\text{X}} \pm n[\mu_{\text{e}} + \Delta V] \quad (2)$$

where X stands for a vacancy: H, BH₄, BH₃, Li, AlH₄, AlH₃ or Na.

For comparison purposes the formation energies of defects presented below are given with respect to the reference solid metal phases (μ_{A}). The chemical potential of hydrogen is fixed at a value calculated for H₂ molecules at $T = 0$ K. For calculation of the formation energies of XH₄ and XH₃ vacancies appropriate X₂H₆ molecules at $T = 0$ K were considered as the reference systems (X = B or Al). Such an approach makes the comparison between two complex hydrides clear-cut and allows focusing on effects related to the charge state of defects.

In the real conditions the defect formation energy will depend not only on the charge state of defects but also on the thermodynamic conditions in which the system is embedded. Thus the formation energy of a given defect depends on the chemical potential of elements constituting a complex hydride ($\Delta H = \Delta H(\mu_{\text{e}}, \mu_{\text{Li}}, \mu_{\text{B}}, \mu_{\text{H}})$ or $\Delta H(\mu_{\text{e}}, \mu_{\text{Na}}, \mu_{\text{Al}}, \mu_{\text{H}})$). Since chemical potentials of elements forming a stable compound are not independent the problem can be simplified [23]. Calculation of defects makes sense only in thermodynamic conditions where complex hydrides are stable, thus for example the stability criterion $\mu(\text{LiBH}_4) \leq \mu(\text{Li}) + \mu(\text{B}) + 4\mu(\text{H})$ has to be fulfilled. In hydrogen rich conditions when hydrides of constituent elements (LiH, NaH, AlH₃, B₂H₆) are more stable than pure metals. Thus the decomposition reactions $\mu(\text{LiBH}_4) \leq \mu(\text{LiH}) + \frac{1}{2}\mu(\text{B}_2\text{H}_6) \leq \mu(\text{LiH}) + \mu(\text{B}) + 3\mu(\text{H})$ and for sodium alanate: $\mu(\text{NaAlH}_4) \leq \mu(\text{NaH}) + \mu(\text{AlH}_3) \leq \mu(\text{NaH}) + \mu(\text{Al}) + 3\mu(\text{H})$ shall be used to determine the limits of the respective chemical potentials. For Ti-related defects at high chemical potential of hydrogen the decomposition products TiH₂, LiH and NaH shall be considered. We have calculated formation energies of all these potential hydride phases. To assess the formation energy of Ti interstitials

in LiBH_4 at the large chemical potential of hydrogen one has to add the energy presented below to the corresponding chemical potential difference between μ_{Ti} and μ_{TiH_2} which equals $\Delta H = 1.55$ eV. For Ti substitution of the cation (central metal in XH_4) the formation energy is larger by $\Delta H = 0.67$ eV (0.9 eV) for LiBH_4 , and $\Delta H = 1.10$ eV (1.48 eV) for NaAlH_4 .

More details about the stability of defects in different thermodynamic conditions for sodium alanate can be found in [14].

3. Assessing accuracy

In the present paragraph we discuss possible sources of errors that are related to the computational approach used in the present studies. The errors related to implementation of DFT methods result from finite sampling of the reciprocal space and finite kinetic energy cutoff. As both LiBH_4 and NaAlH_4 are insulators with large bandgaps, convergence with respect to k -point sampling is fine and accuracy below 0.001 eV per formula unit can be achieved for a k -point grid with density below 0.065 \AA^{-1} (defined as $\max[(k_i \times a_i)^{-1}]$ for k_i sampling along a_i directions; $i = x, y, z$). For calculations of defects with localized gap states a denser grid of 0.05 \AA^{-1} was used. For calculations of the reference metal phases the k -point sampling grid was at least 0.02 \AA^{-1} and for insulating metal hydrides 0.05 \AA^{-1} .

Convergence with respect to the plane wave cutoff is presented in figure 1. Acceptable convergence below 0.005 eV/formula unit is achieved only for the plane wave cutoff of 500 eV for NaAlH_4 and 550 eV for LiBH_4 (potentials used in the present calculations are described in the previous paragraph). These cutoff energies were used in the course of calculations. Figure 1 shows the specific volume of both compounds (inversely proportional to the density), which converges only for high cutoff energies. Relatively slow convergence of the volume and energy is related to a description of negatively charged hydrogen ions present in LiBH_4 and NaAlH_4 . The distance between the central atom and H in MH_4^- molecules converges to 1.638 \AA for NaAlH_4 and 1.223 – 1.228 \AA for LiBH_4 at a cutoff energy of 450 eV and does not change for higher cutoff values. The equilibrium lattice parameters are $a = 4.99 \text{ \AA}$, $c = 11.05 \text{ \AA}$ for NaAlH_4 , and $a = 7.27 \text{ \AA}$, $b = 4.38 \text{ \AA}$, $c = 6.64 \text{ \AA}$ for LiBH_4 . Since the calculated properties and convergence may depend on the choice of potentials for core electrons additional tests were done. The potentials with small core radius (0.42 \AA for H, 0.58 \AA for B, as well as 0.77 \AA for Na with $2s^2 2p^6 3s^1$ electrons treated as valence) give the equilibrium volumes within 1% of those presented above. For these potentials energy convergence below 0.005 eV per formula unit can be achieved for plane wave cutoff energies larger than 875 eV. Thus, for efficiency reasons in the course of this paper we use softer potentials.

In the present approach we use spin polarized calculations because Ti cations can accommodate various multiplet electronic configurations depending on their oxidation state [24]. The gain of the calculated formation energy for Ti substitution of Na in sodium alanate due to the multiplet electronic

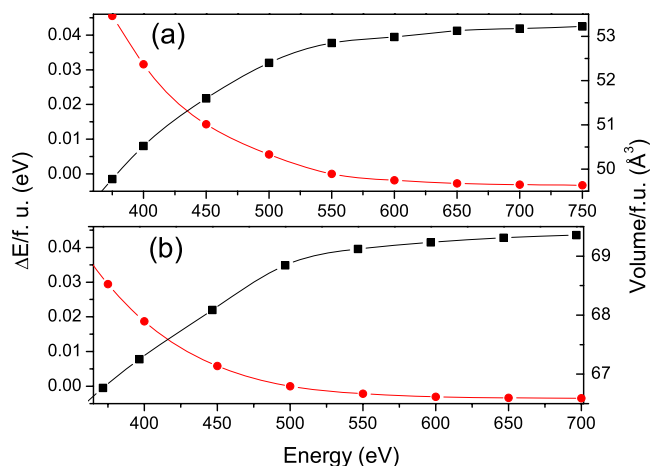


Figure 1. Convergence of the total energy and the volume per formula unit with respect to the plane wave energy cutoff for LiBH_4 (a) and NaAlH_4 (b). (Red) circles are for the energy, black squares are for the volume per formula unit. Lines are guides to the eyes.

configuration of Ti is $\delta E = 0.07$ eV (magnetic moment on Ti $1.5 \mu_B$). For Ti at the Al site $\delta E = 0.11$ eV ($0.75 \mu_B$); for Ti at the interstitial site $\delta E = 0.18$ eV ($0.92 \mu_B$). For LiBH_4 these changes are $\delta E = 0.22$ eV ($1.46 \mu_B$) for interstitial Ti; $\delta E = 0.26$ eV ($1.93 \mu_B$) for Ti substitution for Li and $\delta E = 0.15$ eV ($0.82 \mu_B$) for Ti at the B site. Errors due to omission of spin polarization may thus be substantial and shall not be neglected in restricted calculations.

Approximations and simplification of DFT in the treatment of many-body electronic exchange and correlation effects result in underestimation of the bandgap. This has consequences for calculations of transition levels for charged defects. For example, the bandgap of NaAlH_4 calculated within the GGA approximation equals $E_g = 4.8$ eV, while the GW approach gives $E_g = 6.5$ eV [25]. Various schemes for correction of the bandgap problem exist, including improvement of exchange–correlation functionals [26] and schemes accounting for self-interaction of electrons in DFT [27] or GW methods [28]. These methods, however, are computationally demanding and at present can be applied to rather small systems. Simpler methods that rely on GGA (or local density approximation) calculations (like *scissor*, *extended gap* schemes, etc) are also available [29]. Recent advances in hybrid functionals suggest that the position of the transition level can be calculated within a few percent accuracy when semi-local exchange–correlation functionals (like GGA in the present studies) with suitable band alignment procedures are applied [30]. Nevertheless calculation of exact transition levels is still under development. In the present studies we rely on GGA bandgaps. However, as we compare two compounds errors in transition levels shall not affect the comparison as they apply for both calculations. Moreover, it is not the purpose of the present study to provide accurate transition levels, but rather point out where the differences in interaction of Ti with LiBH_4 and NaAlH_4 are.

One must keep in mind that the band structure and location of the Fermi level in the bandgap has a well-defined meaning for single crystals. Neither lithium borohydride nor sodium

alanate are known to form extended single crystals, even though both compounds are crystalline. Usually micrometer scale grains of both compounds form powders, where each grain consists of numerous single-crystalline domains of nanometer scale. For such systems the position of the Fermi level depends also on the size and surface effects.

Another class of errors is related to the finite size of the supercell used in the simulations and spurious interaction of defects with their periodic images. These errors can be divided into those of elastic origin (they are always present) and of electrostatic nature (present only for charged defects). For the calculations of defect concentration of 6.25% the distance between periodic images is ~ 10 Å for NaAlH₄ and above 7 Å for LiBH₄. Such supercells mimic the real conditions where an isolated defect is embedded into the structure, and elastic relaxation is limited by the strain of the host lattice. In reality, the strain radius can be larger than the distance between periodic images, thus the shape of the cell will effectively change. Test calculations of the influence of relaxation of the supercell for selected defects were performed. To imitate the experimental situation we have optimized the internal atomic positions in the supercell with fixed geometry, then the cell shape and volume was relaxed according to internal stresses, and finally internal atomic positions were re-optimized. For a hydrogen vacancy the error due to elastic interaction is ~ 0.01 eV per formula unit of both NaAlH₄ or LiBH₄. Interstitial titanium results in an error ~ 0.08 eV for NaAlH₄ and ~ 0.06 eV for LiBH₄. For Ti substitution for the central cation in the XH₄ molecule relaxation of the supercell provides an energy gain of 0.1 eV for sodium alanate and 0.12 eV for lithium borohydride. Lovvik and Opalka [11] report somewhat larger relaxation energies of 0.1 eV for interstitial Ti up to 0.15 eV for Ti substitution for Al in NaAlH₄. We believe that differences are due to the relaxation procedure used in our studies.

Change of the supercell shape causes additional errors as it results in changes of the real space grids that are used for calculations of Fourier transforms, and representations of wavefunctions and charge density [31]. For the fixed shape of the supercell these errors are minimized.

Another source of errors is due to long range interactions of point charges related to charged defects. Numerous correction schemes were proposed to minimize such errors [29, 32]. However, there is no general scheme that can be applied for arbitrary system and geometry. Schemes like Makov–Pyne [32] may be strictly applied only for cubic geometries and the accuracy of correction cannot be controlled [29]. On the other hand, for defects with high charges, omission of any corrections may lead to overestimation of the formation energies of those defects [33]. We have decided to apply the linear correction of Makov–Pyne [32] to account for point charge interactions and a possible variety of charge states of defects. The correction energies are: $\Delta E = 0.20, 0.82, 1.84$ and 3.27 eV for charges 1+, 2+, 3+, and 4+ in NaAlH₄, respectively. For LiBH₄ these corrections are: $\Delta E = 0.30$ and 1.20 eV for charges 1+ and 2+, respectively (dielectric constants according to Miwa *et al* [34] for LiBH₄, and Majzoub *et al* [35] for NaAlH₄ were used). Uncorrected formation energy for each defect can be calculated

by subtracting the above correction factors from the values of the formation energies at the valence band maximum.

To summarize, the formation energies of neutral defects are calculated with an accuracy ~ 0.2 eV (finite sampling errors, elastic relaxation errors), while our conclusions are based on energy differences an order of magnitude larger. Transitions levels between +1/0 or 0/−1 charge states are somehow less accurate (~ 0.4 eV, due to electrostatic interaction between defects) yet the energy differences we are focused on are within 2–3 eV. Transition energies between higher oxidation states shall be considered as qualitative only.

4. Results

4.1. Ti-related defects

The insulating character of both materials requires that Ti-related or intrinsic defects shall be considered not only as neutral species but also at various charge states. The formation energies of atomic Ti introduced into the bulk or located on the surface of LiBH₄ and NaAlH₄ are presented in figure 2. In both compounds titanium can be incorporated as an interstitial atom, it may substitute for the cation or central atom in BH₄[−] or AlH₄[−] complexes. For the interstitial sites we report energies for the most stable Ti position. The energy required to introduce Ti as an interstitial or Li substitution into LiBH₄ is always positive (endothermic) and it is almost twice as large as the energy for equivalent defects in NaAlH₄. Li substitution by Ti in the lithium borohydride bulk is energetically favored against Ti interstitials. Only for the Fermi level close to the valence band maximum are Ti⁺¹ cations more stable than neutral Ti atoms. A Ti atom located on the surface is slightly more stable than in the bulk, but it is still highly endothermic. In the bulk of the sodium alanate high oxidation states of Ti are preferred for the Fermi level located close to the valence band maximum, figure 2(b). For this condition incorporation of Ti cations inside NaAlH₄ may be exothermic and the most stable Ti location is at the interstitial position of the crystalline lattice. On the surface the interstitial Ti is less stable than in the bulk, in agreement with data reported in [15]. Charged Ti cations are less stable than neutral ones on the surfaces of both compounds.

Energetics of substitution of the central atom in BH₄[−] and AlH₄[−] complexes are presented in figure 2. For lithium borohydride such a substitution is energetically not favorable. Substitution of Al by Ti in sodium alanate is the most stable process over a large range of the Fermi energy; the formation energy of charge neutral Ti substitution for Al in NaAlH₄ is 1.22 eV, which compares well with previously reported data of 1.27 eV [11] and 1.39 eV [14]. Unlike in previous studies we account for multiplet electronic configurations of Ti. A somewhat lower value of ~ 1.0 eV was reported in [36] where substitution of Al by Ti is discussed in detail; we limit our discussion below to the interstitial Ti and Na/Li substitution by Ti. The formation energy of defects described above can be calculated in different thermodynamic conditions using data in figure 2 and the formalism presented in section 2.

To reveal a reason for the large differences of formation energies of Ti-related defects in LiBH₄ and NaAlH₄ shown

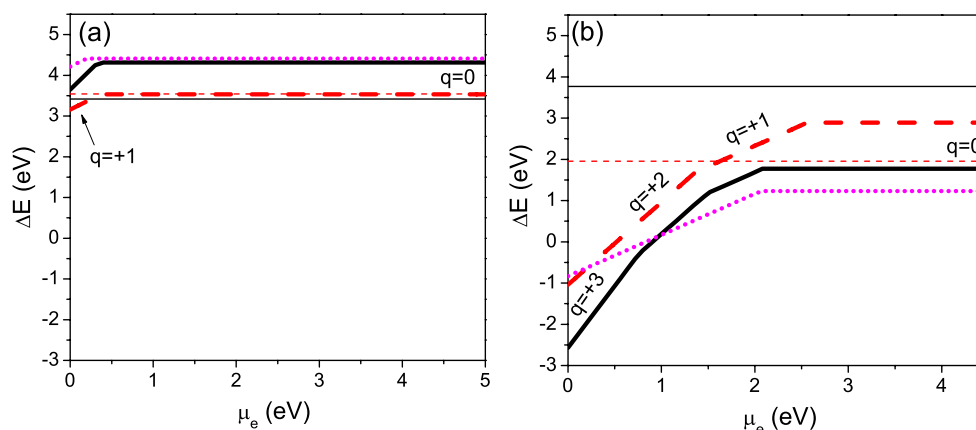


Figure 2. The formation energy of Ti substitutions of Li or Na (dashed line); Ti substitutions of B or Al (dotted line) and Ti interstitial (solid line) in LiBH_4 (a); NaAlH_4 (b). The charge states of defects are denoted as q and marked in the picture. Thick lines are for the bulk, thin ones for the surface. The plots show the formation energy with respect to metallic Ti and conditions of high chemical potentials of other elements involved in defect formation. For the formation energies corresponding to specific thermodynamic conditions, see the text.

in figure 2 the density of electronic states projected on B, Al and interstitial Ti are presented in figure 3. For pure and Ti-doped LiBH_4 there are no electronic states localized on boron atoms in the bandgap. Interstitial Ti exhibits states close to the conduction band minimum (figure 3(a)). The real space projection of the charge density originating from these occupied states is depicted in the insert of figure 3(a). The charge density of neutral Ti interstitial in LiBH_4 lattice is fairly localized (radius ~ 2 Å). In contrast, for the NaAlH_4 introduction of Ti into the lattice induces electronic gap states localized on Al cations, see figure 3(b). The gap states related to Ti extend over a large energy region and the overlap between Al and Ti just above the valence band maximum can be seen. The charge density belonging to these occupied states are shown in the insert of figure 3(b). Significant charge localization between Ti and the nearest Al can be observed.

The doped system must remain charge neutral on the macroscopic scale. To maintain charge neutrality upon introduction of charged defects the charge transfer shall modify the electronic band occupancy or defects with the opposite charge will be formed. Modification of the electronic structure or simply charge transfer between neighboring ions affects valence charges of metal cations and borane or alane molecular units in the vicinity of Ti. Since both compounds are strongly ionic, destabilization/stabilization of atomic charges is an important factor governing the overall stability of the structures [37]. In table 1 valence charges [38] of molecular groups (BH_4 and AlH_4) closest to Ti are presented. For pure compounds Al–H bonds are polarized, as the Bader charge on Al is $+2.18e$, and $-0.76e$ on H. Polarization of the B–H bond is smaller with the charge on B $+1.58e$ and $-0.62e$ on H. Introduction of neutral Ti into the bulk enhances the electron density on BH_4 and AlH_4 groups, which in principle brings molecules closer to the formal oxidation state $-1e$ and stabilizes them [37]. At higher oxidation states of Ti the valence charges on borane or alane groups are more perturbed, see table 1. Significant reduction of charges on BH_4 or AlH_4 may lead to their decomposition already in the bulk. However, Ti in LiBH_4 is highly unstable at high oxidation states and thus

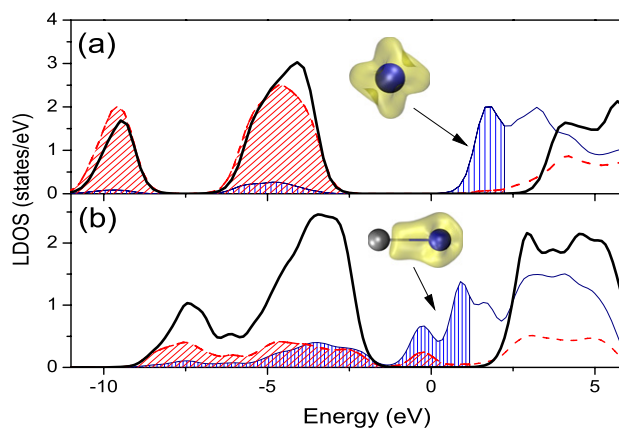


Figure 3. Local density of states LDOS (dashed line) projected on B in LiBH_4 (a) and Al in NaAlH_4 (b) ions that are closest to the neutral interstitial Ti. The DOS (per formula unit) for undoped samples are shown by thick solid lines and LDOS projected on Ti are shown by thin solid lines for reference. The top of the valence bands are aligned with respect to pure complex hydrides; shaded regions indicate occupied states for doped systems. Energy zero is set in the middle of the bandgap of the undoped system. The insert shows the real space projection of neutral Ti gap states. The smaller (blue) sphere is for Ti, larger (gray) for Al.

Table 1. The valence charge for BH_4 and AlH_4 group in the vicinity of Ti impurity in lithium borohydride and sodium alanate. The valence charges for the pure compound are $q = -0.90e$ and $q = -0.86e$ for LiBH_4 and NaAlH_4 , respectively. Charges for highly unstable configurations are printed in italics.

	Ti ⁰	Ti ⁺¹	Ti ⁺²	Ti ⁺³	Ti ⁺⁴
Ti @ I (LiBH_4)	-1.07	-0.91	<i>-0.78</i>	<i>-0.70</i>	<i>-0.52</i>
Ti @ Li (LiBH_4)	-0.92	-0.79	<i>-0.56</i>	<i>-0.32</i>	<i>-0.32</i>
Ti @ I (NaAlH_4)	-0.84	-0.83	-0.72	-0.56	-0.43
Ti @ Na (NaAlH_4)	-0.90	-0.80	-0.71	-0.63	-0.58

decomposition of BH_4 due to the presence of Ti is unlikely. In sodium alanate Ti might reduce the valence charge on AlH_4 such that these molecules decompose already in the bulk.

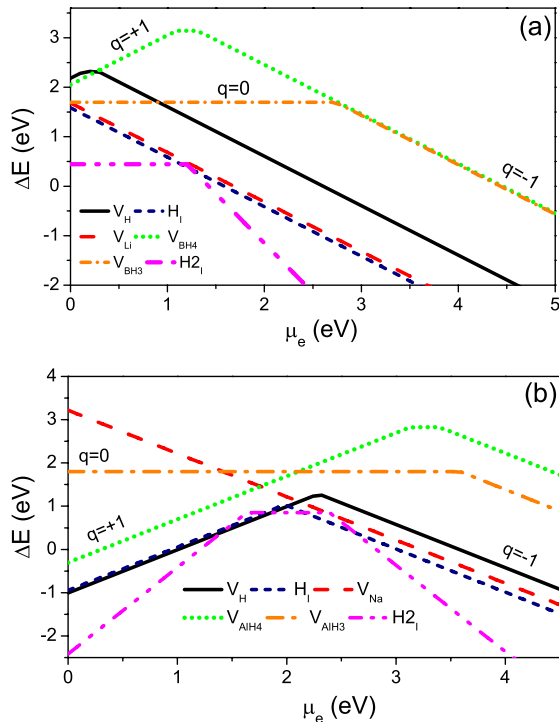


Figure 4. Formation energy of various vacancies and interstitials in LiBH_4 (a) and NaAlH_4 (b). Hydrogen vacancy (V_H) is represented by solid (black) line; dashed (red) line is for Li (V_{Li}) (a) or Na (V_{Na}) (b) vacancy; dotted (green) line for XH_4 vacancy, dashed-dotted (orange) line for XH_3 ($X = \text{B}$ or Al), short dashed (blue) line is for H interstitial (H_I) and dashed-dotted-dotted (fuchsia) for H_2 interstitial (H_{2I}).

4.2. Native defects

Coexistence of Ti-related positively charged defects together with native defects, like vacancies or interstitials with negative charge, would also maintain charge neutrality of the system. The simplest native defects that can exist in the bulk of complex hydrides include H or cation (Li, Na) vacancies, BH_4 or AlH_4 vacancies and atomic or molecular hydrogen interstitials. The formation energy of these defects in LiBH_4 and NaAlH_4 is presented in figure 4. For both compounds charged defects dominate over almost the entire Fermi energy range.

Neither for LiBH_4 nor for NaAlH_4 are neutral atomic hydrogen interstitials (H_I) or hydrogen vacancies (V_H) the most stable in the bulk. The charge state of these defects can change from negative to positive without being neutral. This behavior is characteristic for systems with very strong electron-phonon coupling [39] and known as negative U behavior.

In fact, interstitial H^- in the lattice of NaAlH_4 remains between two AlH_4 , having a slightly shorter bond of 1.78 Å to one and 1.83 Å to another alane group. The interstitial H^+ leads to formation of the H_2 molecule and positively charged hydrogen vacancy V_H^+ [40, 41] (i.e. AlH_3 plus H_2 which is detached from the alane group). A positively charged hydrogen vacancy leads to formation of a ‘hydrogen bond’ between AlH_3 and the nearest AlH_4 (which can also be perceived as Al_2H_7). The distance between a bridge hydrogen and the nearest aluminum ions is 1.69 and 1.84 Å. Thus, charged hydrogen interstitials or vacancies induce large lattice distortion changing locally the coordination number of Al atoms.

In lithium borohydride the most stable hydrogen interstitial exists as H^- , and V_H^- is the most stable charge state of the hydrogen vacancy over the entire energy range, except for a small region just above the top of the valence band, where V_H^+ is most stable, see figure 4(a). This compound also exhibits negative U behavior, but the stability range of positively charged defects is very limited. In figure 5 schemes of the structural relaxations in the vicinity of the hydrogen interstitial and hydrogen vacancy in LiBH_4 are shown. For better comparison between two complex hydrides we show local relaxation of BH_4 groups for interstitial H^+ in figure 5(a), even though this charge state is not stable in the physically meaningful range of the Fermi energy. Similarly to NaAlH_4 in lithium borohydride the H_2 molecule is formed in the vicinity of the interstitial H^+ , but this molecule is bonded to one of the BH_4 groups, not floating freely as in sodium alanate [40]. Interstitial H^- introduces significant rearrangements in the crystal lattice of LiBH_4 . The BH_4 groups surrounding the interstitial H^- relax mainly via semi-rigid rotations. The B–H bonds do not change more than 0.5% from their initial length of 1.22 Å, and the tetrahedral angle is preserved within $\pm 0.9\%$. Also for the hydrogen vacancy (V_H^+) structural

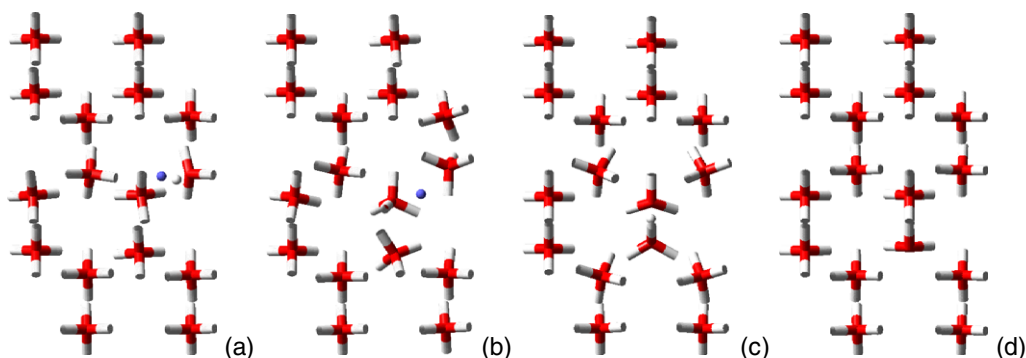


Figure 5. The local structure of LiBH_4 around hydrogen interstitial H^+ (a) and H^- (b). The structure around the hydrogen vacancy V_H^+ is shown in (c) and for V_H^- in (d). The BH_4 molecules are presented by sticks, with dark (red) color for boron atom in the center of the tetrahedron and white ends for hydrogen. The interstitial hydrogen is shown as a blue sphere. Lithium cations are not shown for clarity.

relaxation consists of rigid rotations of BH_4 , see figure 5(c). For this defect B–H bond length modification reaches 1.5% and the BH_4 group is rotated such that the apex hydrogen points towards the exposed boron. For hydrogen-related defects in LiBH_4 the BH_4 groups remain stable entities and boron does not change coordination number for any defect (except hydrogen vacancies) studied in the present work.

From the thermodynamical point of view the introduction of molecular hydrogen (H_2) into the lattice of LiBH_4 and NaAlH_4 is the most facile defect formation process. It has the energy penalty of 0.44 eV and 0.90 eV, respectively. The neutral H_2 interstitial has a relatively large stability region in the bulk of both complex hydrides considered here and diatomic molecules remain stable in the interstitial cavity. At the lower end of the Fermi energy range H_2^{2+} dissociates into two hydrogen ions (H^+), which behave as atomic hydrogen interstitials described above, i.e. each H atom tends to form an H_2 molecule and a positively charged hydrogen vacancy in sodium alanate. In LiBH_4 those molecules are attached to BH_4 groups and no hydrogen vacancies are formed. At the upper end of the Fermi energy range H_2^- dissociates into two H^- ions that again behave as hydrogen interstitials causing reorientation of BH_4 groups or the formation of AlH_5 entities.

For sodium alanate the most stable hydrogen interstitial and hydrogen vacancy can exist in the bulk with positive and negative charges depending on the position of the Fermi level. The transition energy between these charge states is located close to the middle of the bandgap (figure 4). This transition energy is embedded or close to the valence band maximum for LiBH_4 . Such an alignment indicates that for LiBH_4 hydrogen-related defects would serve mainly as acceptor states (taking electrons from the valence band or the occupied gap states).

As the charged H_1 or V_H induce large configurational modifications of BH_4 and changes of the coordination number in AlH_4 groups, the diffusion timescale for hydrogen-related species would be connected to the lattice phonons of LiBH_4 or NaAlH_4 . Even though the position of the Fermi level and the actual charge state of defects cannot be controlled in a real ball milling experiments, it is important to take into account charge transfer and resulting lattice relaxation effects, when studying diffusion in complex hydrides.

Cation vacancies (V_Li and V_Na) with the lowest formation energy are negatively charged in both compounds. The formation energy of the lithium vacancy V_Li^- is much lower than the sodium one, see figure 4. BH_4 vacancies exhibit negative U behavior in the bulk of LiBH_4 , and only a small stability region of neutral AlH_4 exists in NaAlH_4 . Semi-rigid rotations of BH_4 provide the necessary relaxation energy for $\text{V}_\text{BH}_4^+$. In sodium alanate mutual rotation of AlH_4 groups is not present. Positively charged BH_3 and AlH_3 vacancies are not stable in either compound.

According to data presented above a combination of titanium interstitial and sodium vacancy shall be more stable than these defects separately in the charge neutral system. The charge transfer between Ti and V_Na provides an appropriate oxidation state. We have used supercells with 192 atoms for NaAlH_4 and 288 for LiBH_4 to study a combination of Ti interstitial with one and three cation vacancies. Calculations

were performed in a charge neutral supercell. Formation energy of the neutral sodium vacancy in pure NaAlH_4 equals 3.75 eV, increasing to 3.85 eV per vacancy for agglomeration of three V_Na . Such an energy increase indicates effective weak repulsion between vacancies. Formation of Na vacancy in the vicinity of the interstitial titanium atom is lowered to 0.47 eV. Simultaneous formation of three sodium vacancies is even more favorable with a formation energy of -0.01 eV per vacancy.

In lithium borohydride the formation energy of a single neutral Li vacancy equals 4.95 eV, while agglomeration of three vacancies changes this energy to 4.92 eV. The presence of the interstitial Ti lowers the formation energy of V_Li to 0.15 eV for a single vacancy and increases to 0.70 eV for agglomeration of three V_Li . Increase of the formation energy is related to instability of the high oxidation states of Ti in this compound.

Lowering of V_Na and V_Li formation energies in the vicinity of Ti can be explained by the charge transfer from Ti toward cationic vacancy. Effectively vacancies become negatively charged and, as such, they are more stable together with positively charged Ti, see figures 2 and 4.

5. Discussion

The results presented above reveal major differences between LiBH_4 and NaAlH_4 with respect to the interaction with titanium and formation of simple defects that are crucial for understanding the catalytic activity of Ti.

In the bulk of lithium borohydride Ti atoms are highly unstable and the introduction of Ti cations does not affect significantly this situation. As a result only a very low concentration of Ti can be expected inside LiBH_4 . The charge transfer effects or interaction with other charged defects would not be related to incorporation of Ti. Thus the activity of this metal for the decomposition of LiBH_4 is related to surface effects where the stability of Ti is larger than in the bulk.

In sodium alanate incorporation of Ti at high oxidation states can be even exothermic under certain thermodynamic conditions. Positively charged Ti^{n+} cations would interact with other charged defects attracting negatively charged ones. Ti^{n+} in the bulk can be balanced, for example, by n negatively charged Na vacancies, V_Na^- . This effect was already anticipated by Vegge [15], who found that the formation energy of the Na vacancy is strongly reduced in the vicinity of a Ti atom. Our calculations indicate that the energy penalty for creation of a Ti interstitial or a combination of this defect with three sodium vacancies is the same and equals 1.77 eV. Coexistence of V_Na with interstitial Ti locates the Fermi level within 2 eV from the top of the valence band, where positively charged Ti is stable. Upon formation of a Ti-V_Na^- agglomerate a local stoichiometry of TiAlH_n can be formed. These results are in agreement with experimental evidence that TiAl_3 is observed in Ti-doped NaAlH_4 [9]. Moreover they indicate that activity of Ti for NaAlH_4 is not limited to the surface only, but rather effects related to charge transfer and mass transport in the bulk are important.

Charged native defects in sodium alanate cause changes of the aluminum coordination number. In particular positively

charged hydrogen interstitials trigger formation of an H₂ molecule and a hydrogen vacancy. The energy related to this process is relaxed through lattice distortion and the formation of a bridge hydrogen linking two AlH₃ units (formation of Al₂H₇). Indeed recent inelastic neutron scattering experiments report the formation of Al_xH_y species in the bulk of sodium alanate [42]. It was also shown recently that addition of Ti affects a bridge hydrogen inside the bulk of NaAlH₄ [43]. In view of our studies local concentration of positively charged defects related to hydrogen would change since Tiⁿ⁺ cations attract negative defects.

In lithium borohydride negatively charged native defects are energetically preferred over a broad range of Fermi energy, while in sodium alanate positively charged hydrogen vacancies or interstitials can also exist. This originates from different band alignments in both compounds. For LiBH₄ the larger stability of negatively charged defects suggest that additives forming anions could be stable in the bulk. Indeed, addition of amides (NH₂⁻) to LiBH₄ is an already known method improving hydrogen storage and kinetic properties of both compounds [6]. Incorporation of Br⁻ into the bulk of LiBH₄ is also exothermic over a wide range of Fermi energy.

The present calculations concern equilibrium conditions that possibly can never be achieved in the experimental situation for complex hydrides. However, the equilibrium determines the direction of changes in the system that can be hindered by kinetic limitations. They are the subject of our future studies.

The effects related to the charge state of ions in complex hydrides presented above indicate that the application of an electric field would affect kinetic processes in complex hydrides that can be observed in relatively simple experiments.

To summarize, we have presented calculations of simple native and Ti-related defect formation energies in lithium borohydride and sodium alanate. Incorporation of titanium into lithium borohydride is thermodynamically not facile. This process can be exothermic for sodium alanate incorporating Ti³⁺ cations. These results correlate very well with observations that Ti is a good catalyst for NaAlH₄ but not for LiBH₄ and indicate that AlH₄ groups are perturbed by Ti and other charged defects in the bulk of sodium alanate. The BH₄ groups remain intact, irrespective of the presence of defects inside lithium borohydride.

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References

- [1] Schlapbach L and Züttel A 2001 *Nature* **414** 353
- [2] Züttel A, Wenger P, Rentsch S, Sudan P, Fischer P, Mauron Ph and Emmenegger Ch 2003 *J. Power Sources* **118** 1

- [3] 2003 Basic research needs for the hydrogen economy *DOE Report* <http://www.sc.doe.gov/bes/hydrogen.pdf>
- [4] Bogdanović B and Schwickardi M 1997 *J. Alloys Compounds* **253/254** 1
- [5] Anton D L 2003 *J. Alloys Compounds* **356** 400
- [6] Vajo J J and Olson G L 2007 *Scr. Mater.* **56** 829
- [7] Siegel D J, Wolverton C and Ozolinš V 2007 *Phys. Rev. B* **76** 134102
- [8] Au M and Jurgensen A 2006 *J. Phys. Chem. B* **110** 7062
- [9] Streukens G, Bogdanović B, Felderhoff M and Schüth F 2006 *Phys. Chem. Chem. Phys.* **8** 2889
- [10] Léona A, Schildb D and Fichtner M 2005 *J. Alloys Compounds* **404–406** 766
- [11] Løvvik O M and Opalka S M 2005 *Phys. Rev. B* **71** 054103
- [12] Araújo C M, Ahuja R, Guillén J M O and Jena P 2005 *Appl. Phys. Lett.* **86** 251913
- [13] Íñiguez J, Yildirim T, Udovic J, Sulic M and Jensen C M 2004 *Phys. Rev. B* **70** 060101
- [14] Bai K and Wu P 2006 *Appl. Phys. Lett.* **89** 201904
- [15] Vegge T 2006 *Phys. Chem. Chem. Phys.* **8** 4853
- [16] Akbarzadeh A R, Ozolins V and Wolverton C 2007 *Adv. Mater.* **19** 3233
- [17] Yang J, Sudik A, Siegel D J, Halliday D, Drews A, Carter R O, Wolverton C, Lewis G J, Sachtler J W A, Low J J, Faheem S A, Lesch D A and Ozolins V 2008 *Angew. Chem. Int. Edn* **47** 882
- [18] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [19] Kresse G and Joubert J 1999 *Phys. Rev. B* **59** 1758
- [20] Perdew J P *et al* 1992 *Phys. Rev. B* **46** 6671
- [21] Ge Q 2004 *J. Phys. Chem. A* **108** 8682
- [22] Van de Walle C G and Neugebauer J 2004 *J. Appl. Phys.* **95** 3851
- [23] Łodziana Z and Piechota J 2006 *Phys. Rev. B* **74** 184117
- [24] Diserens M J, Smith A C H and Harrison M F A 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 2129
- [25] van Setten M J, Popa V A, de Wijs G A and Brocks G 2007 *Phys. Rev. B* **75** 035204
- [26] Mattsson A E 2002 *Science* **298** 759
- [27] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [28] Kümmel S and Perdew J P 2003 *Mol. Phys.* **101** 1363
- [29] Hedin L 1965 *Phys. Rev.* **139** A796
- [30] Castleton C W M, Hglund A and Mirbt S 2006 *Phys. Rev. B* **73** 035215
- [31] Alkauskas A, Broqvist P and Pasquarello A 2008 *Phys. Rev. Lett.* **101** 046405
- [32] White J A and Bird D M 1994 *Phys. Rev. B* **50** 4954
- [33] Makov G and Payne M C 1995 *Phys. Rev. B* **51** 4014
- [34] He J, Finnis M W, Dickey E C and Sinnott S B 2006 *Adv. Sci. Tech.* **45** 1
- [35] Miwa K, Ohba N, Towata S, Nakamori Y and Orimo S 2004 *Phys. Rev. B* **69** 245120
- [36] Majzoub E H, McCarty K F and Ozoliņš V 2005 *Phys. Rev. B* **71** 024118
- [37] Peles A and Van de Walle C G 2007 *Phys. Rev. B* **76** 214101
- [38] Du A J, Smith S C and Lu G Q 2006 *Phys. Rev. B* **74** 193405
- [39] Henkelman G, Arnaldsson A and Jónsson H 2006 *Comput. Mater. Sci.* **36** 254
- [40] Anderson P W 1975 *Phys. Rev. Lett.* **34** 953
- [41] Peles A and Van de Walle C G 2007 *J. Alloys Compounds* **446/447** 459
- [42] Łodziana Z and Züttel A 2008 *J. Alloys Compounds* doi:10.1016/j.jallcom.2008.03.140
- [43] Fu Q J, Ramirez-Cuesta A J and Tsang S C 2006 *J. Phys. Chem. B* **110** 711
- [44] Kadono R, Shimomura K, Satoh K H, Takeshita S, Koda A, Nishiyama K, Akiba E, Ayabe R M, Kuba M and Jensen C M 2008 *Phys. Rev. Lett.* **100** 026401