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 LiAlH₄ and NaAlH₄ has been carried out using density-functional total-energy calculations. From the theoretical simulations, it is found that both LiAlH₄ and NaAlH₄ are subject to structural phase transitions at high pressure. α-LiAlH₄ transforms to β-LiAlH₄ (α-NaAlH₄-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, LiAlH₄ is predicted to undergo a β-to-γ transition from α-NaAlH₄ to KGaH₄-type structure. α-NaAlH₄ converts to β-NaAlH₄ (SrMgH₄-type structure) at 6.4 GPa with a 4% volume contraction. The high-pressure β phases of both compounds would store hydrogen more volume efficient than the corresponding α 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 β-NaAlH₄ is almost half of that for the α phase, whereas the band gaps for α- and β-LiAlH₄ as 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, MgH₂ 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 (> 250º C).

Recent interest has been directed toward ternary aluminum hydrides owing to their enhanced storage capacity (e.g., LiAlH₄ and NaAlH₄ with 10.6 and 7.5 wt.% theoretical hydrogen content, respectively) as solid-state sources for hydrogen storage (e.g., fuel reservoirs) etc. Hence, LiAlH₄ and NaAlH₄ 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 LiAlH$_4$ and NaAlH$_4$ 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 LiAlH$_4$ and NaAlH$_4$ 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 LiAlH$_4$ and NaAlH$_4$ as explored by first-principle \textit{ab initio} calculations.

**Computational method**

Total energies have been calculated using the projected-augmented plane-wave (PAW) [7] implementation of the Vienna \textit{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 $\alpha$-LiAlH$_4$ and $\alpha$-NaAlH$_4$ we have used 500 and 432 $k$ points,
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; $P6_3mc$) NaGaH$_4$ (orthorhombic; $Cmcm$), NaBH$_4$ (cubic; $Fm3m$), SrMgH$_4$ (orthorhombic; $Cmcm$), 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</th>
<th>Atomic coordinates</th>
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<tbody>
<tr>
<td>$\alpha$-LiAlH$_4$ (prototype; $P2_1/c$)</td>
<td>$a = 4.8535$ (4.8174)$^b$&lt;br&gt;$b = 7.8259$ (7.8020)$^b$&lt;br&gt;$c = 7.8419$ (7.8214)$^b$&lt;br&gt;$\beta = 111.878$ (112.228)$^b$</td>
<td>Li : 0.5699, 0.4652, 0.8245 (0.5603, 0.4656, 0.8266)$^b$&lt;br&gt;Al : 0.1381, 0.2017, 0.9319 (0.1386, 0.2033, 0.9302)$^b$&lt;br&gt;H1 : 0.1807, 0.0986, 0.7630 (0.1826, 0.0958, 0.7630)$^b$&lt;br&gt;H2 : 0.3542, 0.3723, 0.9777 (0.3524, 0.3713, 0.9749)$^b$&lt;br&gt;H3 : 0.2361, 0.0810, 0.1146 (0.2425, 0.0806, 0.1148)$^b$&lt;br&gt;H4 : 0.7948, 0.2633, 0.8717 (0.7994, 0.2649, 0.8724)$^b$</td>
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<tr>
<td>$\beta$-LiAlH$_4$ (α-NaAlH$_4$-type; $I4_1/a$)</td>
<td>$a = 4.6611$ (4.7312)$^d$&lt;br&gt;$c = 10.5219$ (10.7161)$^d$</td>
<td>Li : 0, 1/4, 5/8; Al: 0, 1/4, 1/8 ;&lt;br&gt;H : 0.2527, 0.4237, 0.5413 (0.2492, 0.4191, 0.5429)$^d$</td>
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<tr>
<td>$\gamma$-LiAlH$_4$ (KGaH$_4$-type; $Pnma$)</td>
<td>$a = 6.4667$ (5.4421)$^d$&lt;br&gt;$b = 5.3478$ (4.4843)$^d$</td>
<td>Li : 0.2428, 1/4, 0.2467$^d$ (0.2497, 1/4, 0.2502)$^d$&lt;br&gt;Al : 0.5120, 1/4, 0.8221$^d$ (0.5002, 1/4, 0.7361)$^d$&lt;br&gt;H1 : 0.3067, 1/4, 0.9617$^b$ (0.2815, 1/4, 0.9617)$^d$&lt;br&gt;H2 : 0.7162, 1/4, 0.9631$^b$ (0.7189, 1/4, 0.9467)$^d$&lt;br&gt;H3 : 0.4889, 0.9833, 0.2943$^b$ (0.4998, 0.9173, 0.3279)$^d$</td>
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<tr>
<td>$\alpha$-NaAlH$_4$ (prototype; $I4_1/a$)</td>
<td>$a = 4.9965$ (4.9801)$^e$&lt;br&gt;$c = 11.0828$ (11.1483)$^e$</td>
<td>Na: 0, 1/4, 1/8; Al: 0, 1/4, 5/8;&lt;br&gt;H: 0.2199, 0.3710, 0.5639 (0.2372, 0.3869, 0.5456)$^e$</td>
</tr>
<tr>
<td>$\beta$-NaAlH$_4$ (SrMgH$_4$-type; $Cmcm$)</td>
<td>$a=3.5493$ (3.4047)$^e$&lt;br&gt;$b=13.8304$ (12.9950)$^e$&lt;br&gt;$c=5.1133$ (5.0746)$^e$</td>
<td>Na: 0, 0.1708, 0.2373 (0, 0.1695, 0.2409)$^e$&lt;br&gt;Al: 0, 0.4147, 0.2056 (0, 0.4139, 0.2047)$^e$&lt;br&gt;H1: 0, 0.3485, 0.4807 (0, 0.3476, 0.4877)$^e$&lt;br&gt;H2: 0, 0.3147, 0.0117 (0, 0.3105, 0.0116)$^e$&lt;br&gt;H3: 0, 0.0763, 0.6842 (0, 0.0751, 0.6811)$^e$&lt;br&gt;H4: 0, 0.5232, 0.3816 (0, 0.5269, 0.3739)$^e$</td>
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$^a$ Axes in Å and angles in $^\circ$. $^b$ 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 [AlH₄]⁻ 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 NaAlH₄ crystallizes in the tetragonal structure shown in Figure 1b [12,13]. The [AlH₄]⁻ 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 in the structural stability of LiAlH₄ and NaAlH₄ 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 −50 and +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 LiAlH₄ and NaAlH₄ take the lowest energy (Figure 2a,b) among the seven considered alternatives for each compound. Hence, under ambient conditions LiAlH₄ and NaAlH₄ 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 ±1.5% which is well within the state-of-art limit for density-functional calculation, and also the calculated atomic coordinates for α-LiAlH₄ and α-NaAlH₄ 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 LiAlH₄ and NaAlH₄ as function of pressure. At 2.6 GPa α-LiAlH₄ transforms to β-LiAlH₄ (α-NaAlH₄-type structure) and a subsequent transition from β-to-γ LiAlH₄ (KGaH₄-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 LiAlH₄ modification occurs (probably the γ modification uncovered by the present calculations). Similarly, α-NaAlH₄ transforms to an orthorhombic SrMgH₄-type structure at 6.4 GPa.

The co-ordination number (CN) of Al changes from 4 in α-LiAlH₄ and α-NaAlH₄ to (effectively) 6 in β-NaAlH₄ (6 Al–H distances at 1.678–1.864 Å) and γ-LiAlH₄ (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 AlH₆ coordinations in γ-LiAlH₄ is consistent with reported infrared spectra [15]. At the α-to-β transition point for LiAlH₄ the
The estimated difference in cell volume is ca. 17%. Comparison on the basis of the equilibrium volumes for $\alpha$- and $\beta$-LiAlH$_4$ show an even larger volume difference of some 22%. To our knowledge this is the first observation of such a huge 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 NaAlH$_4$ at the transition point between the $\alpha$ and $\beta$ phases is less than 4% and the involved energy difference of 126 meV f.u.$^{-1}$ is much higher than for LiAlH$_4$.

$\beta$-LiAlH$_4$ deserves special attention. The relatively small equilibrium volume of $\beta$-LiAlH$_4$ 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 $\beta$-LiAlH$_4$ compared with the $\alpha$ phase. In contrast with the situation at the $\alpha$-to-$\beta$ transition point of LiAlH$_4$ both phases have almost the same cell volume at the $\beta$-to-$\gamma$ transition point. Here we are mainly focussing on the unique features of $\beta$-LiAlH$_4$ and $\beta$-NaAlH$_4$ in relation to the corresponding $\alpha$-modifications (see also Refs. 10, 16).

![Graph](image.png)

Figure 2. Pressure-volume relationship for LiAlH$_4$ (left) and NaAlH$_4$ (right). Inset: Gibbs free energy difference with respect to the $\alpha$-phase in as function of pressure. Arrows mark transition pressures.

The calculated density of states (DOS) of the $\alpha$ and $\beta$ phases of LiAlH$_4$ and NaAlH$_4$ are shown in Figure 3. A common feature of these compounds is their nonmetallic character with finite energy gaps above the Fermi level. For LiAlH$_4$ both modifications have almost similar band gaps (4.71 eV for $\alpha$-LiAlH$_4$ and 4.25 eV for the $\beta$-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.

![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.](image)

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-$s$ and -$p$ states appear mainly in region II. The Al-$p$ and H-$s$ states are energetically degenerate in region II, which clearly facilitates the formation of the hybridization prerequisite for the occurrence of the covalently bonded $[\text{AlH}_4]^-$ subunits in the crystal structure (for more details see Ref. 17). When we go from $\alpha$- to $\beta$-LiAlH$_4$ (corresponding for NaAlH$_4$) 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 $\alpha$- and $\beta$-LiAlH$_4$(NaAlH$_4$) whereas the DOSs for Al is markedly different. In $\beta$-LiAlH$_4$ more mixing of $s$ and $p$ states are found for the Al site (see the PDOS for Al in Figure 3). The $s$-to-$p$ electronic conversion for the Al states in the $\beta$-LiAlH$_4$ appears to be the cause of the huge volume collapse at the $\alpha$-to-$\beta$-phase transition.

On going from $\alpha$- to $\beta$-LiAlH$_4$ 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-$p$ with H-$s$ at elevated pressure in NaAlH$_4$, the Al-$p$ peak is shifted from ca. $-1.5$ eV for $\alpha$-NaAlH$_4$ to ca. $-3.5$ eV for the $\beta$ 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 $\alpha$-to-$\beta$ phase transition in this case. The reduction in the band gap and the increase in CN for the $\beta$ 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 $\alpha$ to $\beta$-NaAlH$_4$.

**Conclusion**

The $\alpha$-LiAlH$_4$ and $\alpha$-NaAlH$_4$ transform by application of pressure to $\beta$ modifications at 2.6 and 6.4 GPa, respectively. The estimated volume discontinuity at the $\alpha$-to-$\beta$ transition point is 17 and 4% for LiAlH$_4$ and NaAlH$_4$, respectively. At higher pressure $\beta$-LiAlH$_4$ transforms further to a $\gamma$ modification at 33.8 GPa. The coordination number of Al in $\gamma$-LiAlH$_4$ and $\beta$-NaAlH$_4$ 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 $\beta$-NaAlH$_4$ is only about half of that in the ambient pressure $\alpha$ phase. The involved energy difference between $\alpha$- and $\beta$-LiAlH$_4$ is small and the $\alpha$-to-$\beta$ transition pressure is also relatively low compared to that for the $\alpha$-to-$\beta$ transition of NaAlH$_4$. The low equilibrium volume for the $\beta$ phases of LiAlH$_4$ and NaAlH$_4$ would imply more efficient storage of hydrogen, and with their relatively high weight content of hydrogen the high-pressure $\beta$ phases stands out as promising candidates for hydrogen storage. In $\beta$-NaAlH$_4$, 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 $\alpha$ 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 $\alpha$-to-$\beta$ phase transition in NaAlH$_4$.

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References


