

# Crystal structures and electronic structures of alkali aluminohexahydrides from density functional calculations

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## Abstract

The crystal structure of four bialkali alanates has been calculated by accurate density functional band structure calculations:  $K_2LiAlH_6$ ,  $K_2NaAlH_6$ ,  $KNa_2AlH_6$ , and  $LiNa_2AlH_6$ . The latter hydride has been synthesized previously, but its crystal structure has not been reported before. The former three have previously been shown to be stable. They are all quite similar to the calculated  $Na_3AlH_6$  and  $K_3AlH_6$  structures, which are also presented. The unit cell size and the tilting angle of the  $AlH_6$  octahedra are the largest differences between the structures. Total and local densities of states are presented as well as a Hirshfeld charge analysis for all the stable compounds.

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## 1. Introduction

It is now established that titanium catalyzed sodium tetrahydroaluminate ( $NaAlH_4$ ) is capable of storing up to 5 wt.% hydrogen reversibly at moderate conditions, releasing hydrogen close to the demands from a proton exchange membrane (PEM) fuel cell [1,2]. This system is thus one of the most promising solid state materials for future hydrogen storage applications.

The hydrogen mass density is, however, still not high enough to fulfill the international goals of at least 5 wt.% relative to the whole system, a goal that may become even harder to reach if safety measures are to be included. There is also still a need to improve the kinetics, particularly of the hydrogenation reaction. It is thus important to search for alternative materials that may either improve the hydrogen mass density, the kinetics, or both.

The weight density of H in Li alanates is higher than in Na alanates due to the lighter Li atoms, but the Li alanates have so far not been shown to hydrogenate reversibly [3].

Furthermore, the K alanates have been reported to hydrogenate reversibly without catalysis, suggesting that K may enhance hydrogenation kinetics. This led to our previous work that presented theoretical results suggesting that certain bi-alkali aluminohexahydrides (alanates) on the form  $A_2BAIH_6$ , where A and B are alkali metals, are stable compared to their constituting monoalkali alanates [4].

There has so far not been found any stable bi-alkali alanates on the form  $A_xB_{1-x}AlH_4$ , with A and B being alkali metals [5]. This means that a possible hydrogenation/dehydrogenation scheme would be as follows:



Whether either of these reactions is reversible, that is rehydrogenation from the gas phase is possible, is an open question, and beyond the scope of this work. We present in this paper the full predicted crystal structure of the newly predicted stable phases, together with details from the electronic structure.

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## 2. Computational details

All relaxations and calculations of total energies have been performed by using the Vienna Ab-initio Simulation Package (VASP) [6,7]. We used the Projector augmented wave (PAW) method [8] and the PW91 gradient corrected potential [9] to represent the electron density. The number of points in the  $k$  space integration and the cut-off energy in the plane wave expansions were chosen so that the error in total energy due to these sources was in the order of 1 meV. The criterion for self-consistency was that the total energy differed by less than  $10^{-5}$  eV between two consecutive steps. The structures were relaxed by allowing simultaneous optimization of both ionic positions and cell size and shape, thus avoiding metastable structures. The residual minimization method direct inversion in iterative subspace (RMM-DIIS) implementation of the quasi-Newton algorithm was used in the relaxation, and a final high-precision run was performed using the relaxed structure to calculate the accurate total energy.

The density of states (DOS) plots have been generated by the ADF-BAND program [10,11], which uses a linear combination of numerical and Slater-type atomic orbitals. This makes the local DOS well-defined, without the need to define Wigner–Seitz radii. The number of  $k$ -points and integration accuracy have been chosen to achieve convergence of total

energies within around 10 meV. The basis sets have double zeta quality, and should be quite close to the basis set limit.

## 3. Results and discussion

We have previously predicted that, of the six bialkali aluminates based on Na, Li, and K on the form  $A_m B_n \text{AlH}_6$  ( $m, n = 1, 2$ ), four are thermodynamically stable compared to the monoalkali aluminates:  $\text{K}_2\text{LiAlH}_6$ ,  $\text{K}_2\text{NaAlH}_6$ ,  $\text{KNa}_2\text{AlH}_6$ , and  $\text{LiNa}_2\text{AlH}_6$  [4]. The crystal structures of these compounds are shown in Table 1, and compared to the predicted crystal structures of  $\text{Na}_3\text{AlH}_6$  and  $\text{K}_3\text{AlH}_6$ . To simplify the comparison of the structures, the cell parameters and atomic positions are given in the original  $P2_1/n$  space group. This is also the symmetry resulting from the optimizations, if strict geometrical criteria are applied. The structures are, however, in some cases very close to higher symmetry, and one would expect that the small discrepancies stem from numerical noise. Allowing for such small differences, the  $\text{K}_2\text{LiAlH}_6$  and  $\text{K}_2\text{NaAlH}_6$  structures are recognized as cubic  $Fm\bar{3}m$ . The  $\text{LiNa}_2\text{AlH}_6$  structure is also very close to  $Fm\bar{3}m$ , and almost identical to the recently determined structure from powder neutron diffraction experiments [12]. The  $\text{KNa}_2\text{AlH}_6$  structure has, on the other hand, relatively

Table 1

The predicted crystal structure of the four bialkali aluminates that have been calculated to be stable compared to the calculated crystal structure of Na and K aluminate

$A_m B_n$	$\text{Na}_3$	$\text{K}_3$	$\text{K}_2\text{Li}$	$\text{K}_2\text{Na}$	$\text{KNa}_2$	$\text{LiNa}_2$
Space group	$P2_1/n$	$P2_1/n$	$Fm\bar{3}m$	$Fm\bar{3}m$	$P2_1$	$Fm\bar{3}m$
$a$ (pm)	538.5	602.5	552.8	573.3	557.0	516.5
$b$ (pm)	551.0	610.2	553.6	575.4	564.1	525.1
$c$ (pm)	771.9	858.2	783.2	812.8	797.3	733.9
$\alpha$ (°)	90.00	90.00	90.00	90.00	90.00	90.00
$\beta$ (°)	89.83	89.60	90.03	89.97	89.87	90.03
$\gamma$ (°)	90.00	90.00	90.00	90.00	90.00	90.00
$\delta$ (°)	18.13	12.94	0.78	1.05	15.21	12.48
$A_x$	0.99	0.99	0.00	0.00	0.99	0.00
$A_y$	0.46	0.47	0.50	0.50	0.48	0.00
$A_z$	0.25	0.25	0.25	0.25	0.25	0.50
$B_x$	0.00	0.00	0.00	0.00	0.00, 0.00	0.99
$B_y$	0.00	0.00	0.00	0.00	0.54, 0.00	0.47
$B_z$	0.50	0.50	0.50	0.50	0.75, 0.51	0.25
$\text{Al}_x$	0.00	0.00	0.00	0.00	0.99	0.00
$\text{Al}_y$	0.00	0.00	0.00	0.00	0.00	0.00
$\text{Al}_z$	0.00	0.00	0.00	0.00	0.98	0.00
$\text{H}_1x$	0.09	0.06	0.00	0.00	0.04, 0.92	0.07
$\text{H}_1y$	0.04	0.02	0.00	0.00	0.01, 0.97	0.02
$\text{H}_1z$	0.22	0.20	0.23	0.22	0.21, 0.77	0.23
$\text{H}_2x$	0.23	0.26	0.27	0.28	0.25, 0.76	0.23
$\text{H}_2y$	0.33	0.33	0.27	0.29	0.32, 0.69	0.30
$\text{H}_2z$	0.54	0.53	0.50	0.50	0.55, 0.49	0.53
$\text{H}_3x$	0.16	0.16	0.23	0.21	0.17, 0.81	0.20
$\text{H}_3y$	0.27	0.24	0.23	0.22	0.25, 0.75	0.27
$\text{H}_3z$	0.94	0.96	0.00	0.00	0.95, 0.02	0.96

The compounds are on the form  $A_m B_n \text{AlH}_6$ . For the sake of comparison, all the structures have been shown in the lowest symmetry, that is with the highest precision of the symmetry recognition. All the structures except that of  $\text{KNa}_2\text{AlH}_6$  are then recognized as  $P2_1/n$ . With lower precision of the symmetry recognition (comparable to the precision of our method), the structures are recognized in the listed space groups. In addition to the cell parameters, the tilting angle  $\delta$  of the  $\text{AlH}_6$  octahedra relative to the  $c$  axis has been shown.

low symmetry, and the 4e positions of  $P2_1/n$  are thus split into two non-equivalent 2a positions in  $P2_1$ .

The largest difference between the structures is found for the lattice constants, which change by up to 10% between the largest ( $K_2NaAlH_6$ ) and smallest ( $LiNa_2AlH_6$ ). Apart from this, there are only small differences. All the structures have  $\alpha = \gamma = 90^\circ$ , and  $\beta$  is within  $0.4^\circ$  from  $90^\circ$ . Al is placed at (0,0,0) for all the models except  $KNa_2AlH_6$ , in which Al has been displaced by approximately 17 pm. One of the alkali atoms is also always at  $(0,0,\frac{1}{2})$ , again with  $KNa_2AlH_6$  as the exception, as one sodium atom is displaced by some 8 pm. All the models have been checked with both the smallest and the largest alkali atoms at the  $(0,0,\frac{1}{2})$  site, and the most stable configuration was in all the cases with the smallest atom at that site. The other alkali atom is placed at the  $(0,\frac{1}{2},\frac{1}{4})$  site in the  $K_2LiAlH_6$  and  $K_2NaAlH_6$  structures, while it is slightly displaced from this in  $LiNa_2AlH_6$  and  $KNa_2AlH_6$ , similar to in  $Na_3AlH_6$  and  $K_3AlH_6$ . The three hydrogen positions are equivalent (to within less than 8 pm) in the  $K_2LiAlH_6$  structure, and the two last hydrogen positions are equivalent (to within around 8 pm) in the  $K_2NaAlH_6$  structure. In the other structures the three hydrogen positions are distinctly different. This is due to the  $AlH_6$  octahedra being tilted away from the  $c$  axis for these structures. The tilting angles are listed in Table 1, and we see that the octahedra only are tilted around  $1^\circ$  in the two almost cubic structures ( $K_2LiAlH_6$  and  $K_2NaAlH_6$ ), while they are tilted by between 12 and  $18^\circ$  in the other structures. Since the bialkali alanate structures all are quite similar to both the  $Na_3AlH_6$  and  $K_3AlH_6$  structures (which are distinctly different from the  $Li_3AlH_6$  structure), there is no reason to believe that they should have worse hydrogenation kinetics, at least as long as the crystal structure is of any significance for the kinetic properties.

The total and local DOS are shown for the four stable bialkali alanates and compared to the three monoalkali alanates in Figs. 1 and 2, respectively. Apart from  $Li_3AlH_6$ , all the compounds show three distinct valence bands and one relatively broad conduction band. The s, p, and d orbitals of Al are primarily occupying the lowest, middle, and highest valence bands, respectively, while the bands all contain all types of alkaline and H electrons. The three valence bands are highest and most narrow for  $K_3AlH_6$ , while the two highest bands are grown together for  $Li_3AlH_6$ . The bialkali alanates are to a certain degree interpolating their constituting monoalkali alanates, but with several exceptions. Both the two K–Na alanates, for example, have a broader upper valence band than those of both Na and K alanate, while the second band is broader than that of K alanate, and smaller than that of Na alanate. The two upper bands of K alanate have both two distinct peaks, whereas this is split into four peaks in the second band of Na alanate. This is partially reflected in the K–Na alanates, which have a small third peak in their middle valence band. The lowest valence band is located at almost the same place for both the K–Na and pure Na alanates, around 0.5 eV lower than for K alanate. The conduction band of  $Na_3AlH_6$  is somewhat broader than for  $K_3AlH_6$ , and it

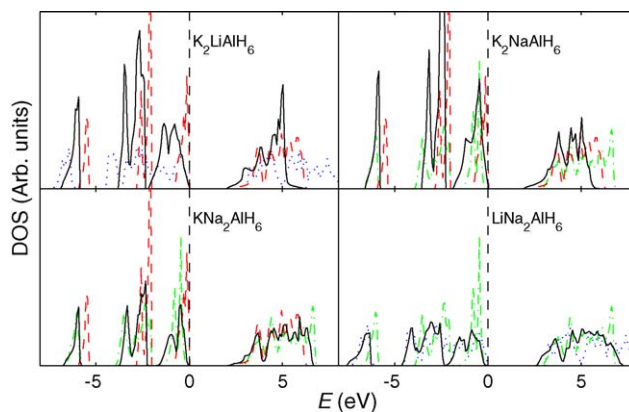


Fig. 1. The total density of states (DOS) of  $K_2LiAlH_6$ ,  $K_2NaAlH_6$ ,  $KNa_2AlH_6$ , and  $LiNa_2AlH_6$  (solid curves). They are compared to the total density of states of  $Li_3AlH_6$  (blue dotted curves),  $Na_3AlH_6$  (green dash-dotted curves) and  $K_3AlH_6$  (red dashed curves). The energy is in eV relative to the Fermi level. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

also has more complex structure. The DOS of  $KNa_2AlH_6$  is most similar to  $Na_3AlH_6$ , while that of  $K_2NaAlH_6$  is most similar to  $K_3AlH_6$ . The band gap is around 3 eV for all the three monoalkali alanates, while it is only 2 eV for the three bialkali alanates containing K. In the bialkali systems, the differences in the electronegativities of the different alkali metals lead to a polarization which reduces the Madelung potential and hence the band gap. The two bialkali alanates containing lithium both have three valence bands, but the two uppermost ones almost coincide, and in  $Li_3AlH_6$  they are completely coalesced.  $LiNa_2AlH_6$  has achieved much of the complex structure similar to that of  $Li_3AlH_6$ , while  $K_2LiAlH_6$  has only two distinct peaks, like  $K_3AlH_6$ , but in addition also a small extra peak in the second and third bands.

One of the most interesting properties of the alanates is their ability to reversibly store hydrogen. For the alkali alanates the trend is quite clear: Li alanates are difficult or impossible to hydrogenate from the gas phase, Na alanates are reversible after catalyzing with transition metals, while K alanates are reversible even without catalysis [13]. It is not yet possible to understand this properly from the detailed electronic structure, but we observe that there is a clear trend from the complex electronic structure of Li alanate to the very clean picture of K alanate. If this is relevant for the hydrogenation properties of the alanates, the complexity of the electronic structure of the bialkali alanates may be a sign of their possible reversibility. In that case, the hydrogenation properties of  $LiNa_2$  alanate should be between those of the Li and Na alanates, while all the three stable bialkali alanates containing K are between Na and K alanate in complexity. The former is thus an interesting alternative with relatively low weight, and the latter ones could, if the addition of K is of any importance in this respect, have better kinetics than  $Na_3AlH_6$  without seriously compromising the hydrogen weight density.

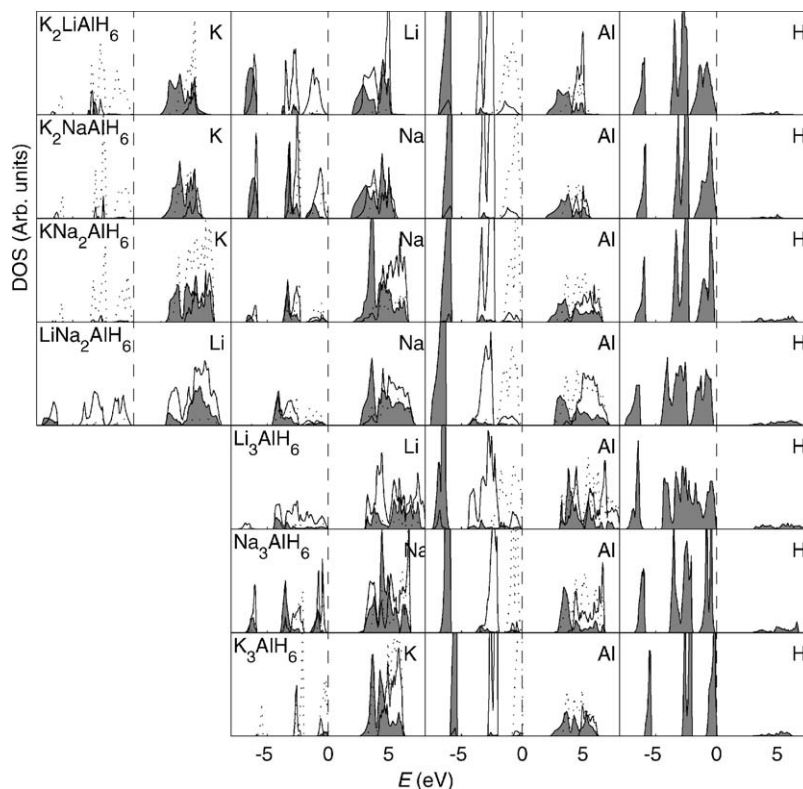


Fig. 2. The local DOS projected on the s (shaded grey), p (solid lines), and d (dotted lines) orbitals of the specified atoms for the bialkali aluminates.

Table 2  
Hirshfeld charges for the different materials

$A_mB_n$	Li <sub>3</sub>	Na <sub>3</sub>	K <sub>3</sub>	K <sub>2</sub> Li	K <sub>2</sub> Na	KNa <sub>2</sub>	LiNa <sub>2</sub>
$q_A$	0.16	0.24/0.26	0.34/0.30	0.33	0.33	0.32	0.12
$q_B$	–	–	–	0.12	0.21	0.28/0.22	0.26
$q_{Al}$	0.27/0.24	0.16	0.11	0.15	0.12	0.14	0.19
$q_H$	–0.12	–0.15	–0.18	–0.15	–0.16	–0.15/–0.17	–0.14
$q_{AlH_6}$	–0.48	–0.75	–0.97	–0.76	–0.86	–0.82	–0.64

Where two values are given, they represent the noted atom in different crystallographic positions. The compounds are on the form  $A_mB_nAlH_6$ .  $q_{AlH_6}$  denotes the sum of the charges for the aluminide ion. The monoalkali aluminates are included for comparison.

Hirshfeld population analyses for the systems under study are summarized in Table 2. These atomic charges serve to illustrate the ionic part of the interaction, which is important for the presently studied aluminates. On inspection of the atomic charges, we note that lithium is significantly less cationic than sodium or potassium, a result which is in line with the fact that lithium is a small atom of relatively low polarisability, and that it has a higher ionization energy and a lower Pauling electronegativity than sodium and potassium. These differences are also borne out by the entirely different structure for  $Li_3AlH_6$  compared to the structures presented here (it has  $R\bar{3}$  symmetry), and the fact that the lithium-rich bialkali aluminates not included in the present report ( $Li_2NaAlH_6$  and  $Li_2KAlH_6$ ) are unstable with respect to their constituting monoalkali aluminates. The larger alkali atom is the most cationic in each case, a fact which may be explained along the same lines.

The anionicity of hydrogen appears to be only weakly dependent on the alkali metals. A consequence of this is that the atomic charge of aluminium depends strongly on the alkali metal atoms present. Viewing the aluminide anion as a single entity, it reflects the cationicity of the alkaline ions, increasing from Li to K aluminate with the bialkali aluminates interpolating. These results are consistent with the local DOS and the crystal structures; all the investigated properties of the currently studied hypothetical bialkali aluminates interpolate those of the corresponding monoalkali aluminates.

#### 4. Conclusions

The detailed crystal structure and electronic density of states have been presented for the four bialkali aluminates  $K_2LiAlH_6$ ,  $K_2NaAlH_6$ ,  $KNa_2AlH_6$ , and  $LiNa_2AlH_6$ . The

three former compounds have not yet been synthesized, but was predicted to be stable in a previous study [3]. The predicted crystal structures of these compounds are quite similar, with the unit cell size and the tilting angle of the hydrogen octahedra being the largest difference between the structures.

The calculated DOS show a decreasing degree of complexity when moving from the light aluminates towards the heavier ones, with the bialkali aluminates interpolating the behaviour of their constituents. The same is also seen when calculating the charge transfer between the atoms by a Hirshfeld population analysis; the charge transfer in the bialkali aluminates interpolates that in the corresponding monoalkali aluminates. We would like to encourage experimentalists to investigate whether the hydrogenation kinetics of bialkali aluminates also interpolates between those of the monoalkali aluminates.

#### Note added in proof

$K_2LiAlH_6$  and  $K_2NaAlH_6$  have now been synthesized, [J. Graetz, Y. Lee, J. J. Reilly, S. Park, T. Vogt, *Phys. Rev. B* 71 (2005) 184115] and their crystal structures are very close to the predicted ones.

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