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, $Fm3m$)[12], SrMgH$_4$ (orthorhombic; $Cm21$)[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-
Results are obtained using projector-augmented plane wave (PAW) potentials provided with the VASP. The ions are relaxed toward equilibrium 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. All calculations are performed with 600 $k$ points in the whole Brillouin zone and 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 [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 $a = 9.009$, $b = 5.767$, $c = 7.399$ Å at 0 K 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 Å$^3$/f.u., respectively). Table 1 therefore also

Fig. 1. Structural competition between different possible structural arrangements for KAlH$_4$.

Fig. 2. (a) The ground-state crystal structure of KAlH$_4$. (b) The slightly distorted $[\text{AlH}_4]^{-}$ tetrahedron with the interatomic Al–H distances (in Å).
Table 1
Optimized structural parameters, bulk modulus ($B_0$), and the derivative of bulk modulus ($B'_0$) for KAlH₄

<table>
<thead>
<tr>
<th>Unit-cell dimensions (Å)</th>
<th>Space group</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGaH₄ type:</td>
<td></td>
<td>K (4c): 0.1778, 1/4, 0.1621</td>
<td>10.34</td>
<td>4.61</td>
</tr>
<tr>
<td>a = 9.009 (8.814) Å</td>
<td></td>
<td>Al (4c): 0.5663, 1/4, 0.8184</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b = 5.767 (5.819) Å</td>
<td></td>
<td>H1 (4c): 0.4034, 1/4, 0.9184</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c = 7.399 (7.331) Å</td>
<td></td>
<td>H2 (4c): 0.7055, 1/4, 0.9623</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>H3 (6d): 0.4194, 0.9810, 0.3127</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>H3 (6d): 0.4194, 0.9810, 0.3127</td>
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<tr>
<td></td>
<td></td>
<td>Al (4b): 0, 1/4, 0.78</td>
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<td></td>
<td></td>
<td>H1 (16f): 0.2500, 0.3543, 0.5409</td>
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<td>a = 5.442</td>
<td></td>
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<td></td>
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<tr>
<td>c = 12.661</td>
<td></td>
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</tbody>
</table>

* From XRD measurements [8].

The calculated cell volume for the KGaH₄-type ground-state variant is in very good agreement with the observations, remembering that the calculations refer to 0K and the experimental values to room temperature, and moreover that GGA calculations [20] usually overestimate cell volumes. In this case the deviation between the calculated and observed unit-cell dimensions is 2.2% in $a$, −0.9% in $b$, 0.8% in $c$, and 2.2% in $V_0$.

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-

![Experimental and Calculated XRD Patterns](image)

Fig. 3. Experimental [7] and theoretically simulated XRD patterns for KAlH₄ (Cu Kα₁ radiation; normalized with equal peak intensity for the reflection at $2θ \approx 25^\circ$). Two peaks attributed to unreacted aluminium in the original experimental diffractogram are omitted from the comparison.
perature on a sample burdened with defects and impurities. An ongoing experimental study [21] on KAlH$_4$/KAlD$_4$ 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.

KAlH$_4$ is isostructural and isoelectronic with KGaH$_4$, whereas other isoelectronic compounds like NaAlH$_4$ and NaGaH$_4$ take rather different crystal structures (see Section 1). The KAlH$_4$ ground-state structure consists of slightly distorted [AlH$_4^-$] tetrahedra (Fig. 2b) which are separated by intermittent K$^+$ cations (Fig. 2a). The interatomic Al–H distance (see Fig. 2b) within the [AlH$_4^-$] 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 3.204 Å. The $\alpha$-NaAlH$_4$-type structures of the proposed metastable modification of KAlH$_4$ also comprise tetrahedral [AlH$_4^-$] 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 KGaH$_4$- and $\alpha$-NaAlH$_4$-type structures of KAlH$_4$ are fitted with the so-called universal equation of states [23] to derive the bulk modulus ($B_0^0$) and its derivative ($B_0^{\prime}$). The thus obtained small values (Table 1) show that KAlH$_4$, like the isoelectronic analogues LiAlH$_4$ ($B_0^0$ = 12.95 GPa [24]) and NaAlH$_4$ ($B_0^0$ = 19.30 GPa [10]), is a very soft and easily compressible material.

4. Density of states

The calculated density of state (DOS) for KAlH$_4$ in the KGaH$_4$-type structure is displayed in Fig. 4. From the total DOS in the lower panel it is clear that KGaH$_4$-type KAlH$_4$ has a non-metallic character with a band gap of ca. 5.5 eV, which is close to the band gaps in other technologically interesting hydrides, viz. MgH$_2$ (4.3 eV [19]), LiAlH$_4$ (4.8 eV [24]), and NaAlH$_4$ (5.04 eV [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 $-3.9$ to $-3.5$ eV and another at $-1.8$ to 0 eV. 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: 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 [AlH$_4^-$] complex.

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References