



Density Functional Studies on Crystal Structure of Potassium Alanates as a candidate for Hydrogen storage

Samira Adimi^a, Hadi Arabi^{a,*}, Faiz Pourarian^b

^a*Department of Physics, Ferdowsi University of Mashhad, Iran*

^b*Applied Advanced Technologies, Carnegie Mellon Research Institute, USA*

**Corresponding Author's E-mail: (arabi-h@um.ac.ir)*

Abstract

Potassium alanate has been one of the goal candidates for hydrogen storage during past decades. In this report, we used Density Functional Theory to reproduce the structural parameters for experimentally known KAlH_4 within the accuracy of 0.01% by relaxing the structure with total force less than 0.001eV per unit cell. The final deduced cell parameters were $a=8.834$, $b=5.763$, $c=7.328$. All calculations were carried out by using projected augmented plane wave method via Quantum espresso package. From the density of states together with band structure, we found that this material has nonmagnetic insulator characteristics with a band gap of 5.1 eV.

Keywords: Hydrogen storage materials, Alanate, complex Hydrides, Density Functional Theory

1. Introduction

The significant challenge for on-board applications of Hydrogen energy is the lack of ideal storage material, especially for practical and economical usages. Hydrogen can be stored in three different shapes: gaseous, liquid and inside the bulk of a solid-state material. Hydrogen Gas and liquid forms have several disadvantages such as occupying large volume and high cost, respectively. So the storage of Hydrogen in solid-state form was the most preferable way till now. However, the solid-state materials has its problem too.

The target of US Department of Energy (DOE) for a suitable material for storage until 2017 is gravimetric of 5.5Wt% H_2 and volumetric of 40 g/L [1] for hydrogen absorption temperature between 40-85°C at the pressure of 1bar which means that formation energy of this material should be in the range of -30 to -48kJ/mol H_2 [2] to meet requirement condition for fuel-cell powered vehicles. However no single material has met all these conditions yet and development of a high volumetric and gravimetric hydrogen storage material with fast de/rehydrogenation speed was the subject of significant efforts in this technology during several past decades.

In the wide range of available options for on-board Hydrogen storage, metal complex hydrides have potential to be used as efficient hydrogen storage due to their high purity of released H_2 [7], light weights, low costs, high hydrogen capacities (7.5 wt.% for NaAlH_4 , 10.6wt% for LiAlH_4 and 5.7wt% for KAlH_4) and moderate decomposition temperature.



In the center of studies in recent years was Sodium Alanate which Bogdanovic and Schwichard showed that it has reversibility at moderate pressures and temperatures after adding titanium compound as a catalyst [3].

This discovery sparked a lot of interest toward hydrides and a lot of researches were done for decomposition of LiAlH_4 which theoretically contains 10.6Wt% hydrogen. Unfortunately, dehydrogenation of this material requires more than 400°C of temperatures and a pressure above 10000 bar [4] without presence of any catalyst, so this compound definitely is not suitable for transport purpose. Adding suitable catalyst will lower pressure and temperature so much, but not as much as needed. Anyway the exact mechanistic and reactions of alanates with hydrogen and the role of additive are not fully understood yet and is a major problem in theoretical studies of complex hydrides.

Potassium alanate has a very similar structure with Lithium and Sodium alanates but experimental reports show that there is a main advantage of KAlH_4 over them: reversibility of hydrogen without need to any additional additive at moderate temperatures ($250\text{-}300^\circ\text{C}$) and low pressures ($<1\text{MPa}$).

Nevertheless, the main obstacle for practical application of KAlH_4 is slow dehydrogenation kinetics of Hydrogen that will be reflected in high pressure and temperature of forward and reverse processes.

Few theoretical studies have been done to understand the structural properties of KAlH_4 . Firstly, Vajeeston et al. had considered seven close structural types [5] to predict the ground structure of KAlH_4 by applying of DFT calculation implemented with Vienna ab initio simulation package (VASP) [6] to show that an orthorhombic structure with KGaH_4 -type form has the minimum total energy among others.

Understanding the reversibility mechanism in KAlH_4 , might guide us to obtain similar improvement with other alanates so we can use this material as a model system to understand hydrogen storage formalism and find better catalyst resulting to speed up kinetics of reaction.

However, finding the crystal structure of Potassium alanate by experimental methods is not easy. The reasons are among low scattering power of Hydrogen in obtaining hydrogen positions by use of X-ray diffraction, difficulty of synthesizing sufficiently large crystals and usual structural complexity of hydrides.

In this study, due to high motivation have brought about from this subject, we reported crystal, electronic structures and heat of formation of KAlH_4 by using Density Functional Theory (DFT) calculation method, which exhibits an insulator characteristic with a calculated energy band gap of 5.1 eV.



2. Computational methods

Our calculations for structural relaxation and electronic properties were performed based on Density Functional Theory (DFT) [7] in a basis set of plane waves with the Projector Augmented Wave (PAW) pseudo-potentials for electron-core interactions [8] as implemented in Quantum Espresso Package [9]

The atomic valance electrons involved were $3s^2 3p^1$ for Al, $1s^1$ for H and $3s^2 4s^1 3p^6$ for K, respectively. We used an orthorhombic unit cell, with Pnma space group, determined by Joes R. Ares et al. [10] in room temperature by using of X-ray diffraction pattern for starting calculation. Then the structure was fully relaxed by allowing both ionic positions and lattice parameters to be changed, until the residual forces on each atom is less than 10^{-3} ev. The cutoff energy was 40 Ry in all calculations and a $6 \times 8 \times 6$ k-point mesh, generated by the MontkhorstePack method was used to sample the first Brillouin zone [11]. Convergence threshold (criterion) of self-consistent energy was less than 10^{-4} a.u per unit cell and the BFGS quasi-newton algorithm [12] was used to calculate the ground state geometry of structure.

3. Results and discussion

3.1 Crystal structure

The optimized geometry of complex hydride $KAlH_4$, which is crystalized in the orthorhombic structure, is shown in Figure 1. The lattice parameters and its cell volume are compared with the experimental result in Table1. Furthermore, we present and compare our simulated results with that of some previous theoretical works in table 2, which clearly indicates that our results almost coincident to their values. Due to the absent of total energy in the references, we calculated the total energy of their structures and found that our relaxation procedure ends up to a structure with lower energy. The calculated unit cell in zero temperature is in good agreement with the experimental work. The Wyckoff positions of K, Al and H atoms in $KAlH_4$ has been calculated and are reported in table 3.

The relax structure has slightly distorted $[AlH_4]^-$ blocks, shown in Figure 2. which is separated by K^+ cations and final enthalpy was reached to -629.07 Ry. The distance of Al-H bonds vary between 1.627-1.637 Å. Each Potassium ion is surrounded by 12 atoms of Hydrogen and the distances are changed from 2.667 to 4.982 Å.

3.2 Electronic properties

The total Density of States (DOS) of $KAlH_4$ and partial electronic DOS for each atomic species (K, Al, H), in the optimized structure, are plotted in Figure 3. The Fermi level is set in zero energy. In all partial DOS plots s-states are shaded and $3s^1$ states of Potassium are dotted.



It is obvious that valence band is occupied with s and p orbitals of Aluminum and s orbital of Hydrogen and conduction band is occupied with Al and K orbitals. The partial DOS of Al shows quite separation of Al-s and Al-p states but these states are energetically mix in K-pDOS. Since Al-p and H-s states are in the same range of energy they are very suitable to form a hybridized sp orbitals and have a covalent bonds which could lead to form a $[AlH_4]^-$ group. The contribution of outer s orbital of Potassium in the valence band is so small, thus we expect non covalent interaction between K and AlH_4 blocks. The total DOS shows an insulator behavior of Potassium alanate with energy gap of 5.1 eV. Main contribution of the peak with -2 to zero eV energy is from orbital s of Hydrogen and orbital p of Aluminum and the next peak with almost -3.5 to -5 eV energy arise from contribution of s orbitals of Al and H.

Figure 4. shows the calculated band structure along high symmetry directions $\Gamma(0,0,0)$ to $R(0.5,0.5,0.5)$. We know that there is dependency of electronic energy to k-vectors along the high symmetry directions in Brillouin zone so interesting information such as optical absorption and band gap of the materials can be deduced from band structure plots [14].

At Γ point the difference between valence bands and conduction bands is 5.02eV which is a rough estimate of $KAlH_4$ bandgap.

4. Conclusions

In this investigation, the structural and electronic properties of $KAlH_4$ have been simulated using DFT method via Quantum espresso package. Our calculated structural parameters are in good agreement with experimental results. The density of states and band structure of $KAlH_4$ indicated that this material is an insulator and Al-H bonds has a covalent nature.

Table 1. The experimental unit cell geometry of $KAlH_4$

a(Å)	b(Å)	c(Å)	Cell volume	References
8.858	5.822	7.352	328.8	10
8.834	5.763	7.328	-620.0738	This work

Table 2. Simulated unit cell and self-consistent energy of $KAlH_4$

a(Å)	b(Å)	c(Å)	E_{scf}	Total Force	References
9.009	5.767	7.399	-629.0487	0.1084	5
8.814	5.819	7.331	-629.0709	0.044	13
8.834	5.763	7.328	-620.0738	0.001	This work

Table 3. Optimized atomic position of $KAlH_4$

Atom	site	positions		
Al	4c	0.5694	0.250	0.8196
K	4c	0.1778	0.250	0.1621
H	4c	0.4071	0.250	0.9247
H	4c	0.9059	0.250	0.5745
H	8d	0.5815	0.4783	0.6882

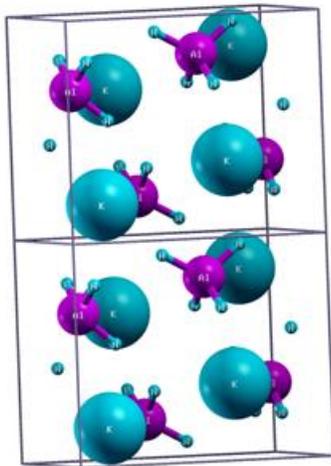


Fig1. The crystal structure of $KAlH_4$

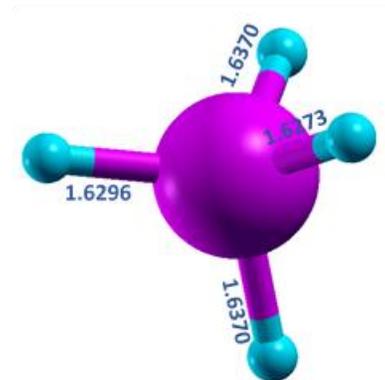


Fig2. The bond length of AlH_4 Block

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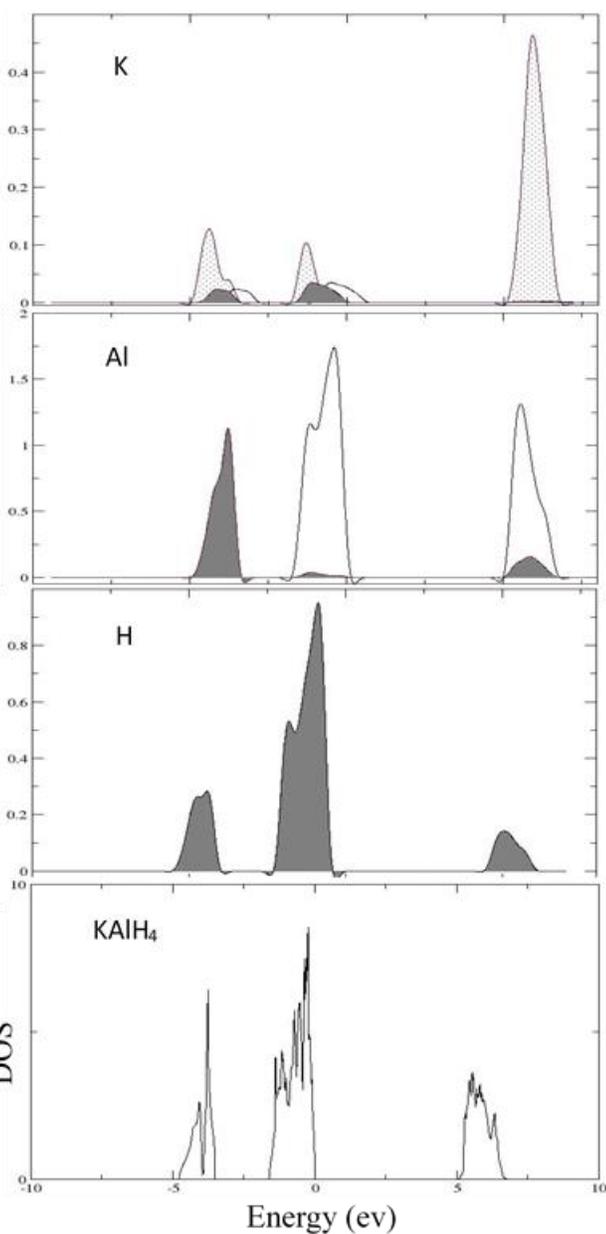


Fig3. Calculated DOS and the Projected DOSs for KAlH₄

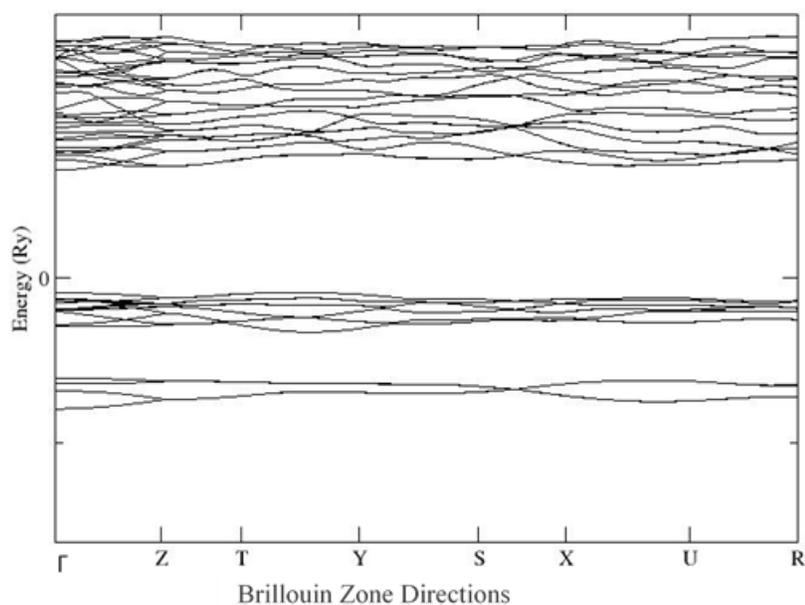


Fig4. Band Structure of KAlH₄ in specified direction



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