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Theoretical modeling of hydrogen storage materials: Prediction of structure, chemical bond character, and high-pressure behavior

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Abstract

Density-functional theory (DFT) is a powerful tool to predict crystal structure, chemical bond character, and high-pressure behavior of materials. In this report, we show the application of DFT to study such properties for complex hydrides. The structural parameters for the experimentally known Li_3AlH_6 phase have been successfully reproduced within an accuracy of less than 1% and the crystal structure of $KAlH_4$ has been predicted. From examination of the density of state, we find that these materials have insulating behavior with a band gap of ∼3.5 and 5.5 eV for Li_3AlH_6 and $KAlH_4$, respectively. From analyses of charge density, charge transfer, electron localization function, crystal orbital Hamilton, and Mulliken population we find that the interaction between Li/K and $[AlH_4]$/$[AlH_6]$ is essentially pure ionic, whereas within the $[AlH_4]$/$[AlH_6]$ unit the interaction is partially ionic and partially covalent. Even though these materials are very soft the Al–H interaction is relatively strong compared with the other interactions. Subject to external pressure the equilibrium structure of Li_3AlH_6 is unstable. We predicted that this compound undergoes three successive structural phase transitions under pressure: α to β at 18.64 GPa, β to γ at 28.85 GPa, and γ to ϵ at 68.79 GPa. $KAlH_4$ is stable and no pressure induced structural transitions were identified.
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Keywords: Complex hydrides; Theoretical modeling; Structural stability; Chemical bond character; High-pressure behavior

1. Introduction

High capacity solid-state storage of hydrogen is becoming increasingly important for fuel cells, automotive, and electrical utility applications. Compared to liquid hydrogen one of the major drawbacks of known reversible metal hydrides applicable for hydrogen storage is their low gravimetric hydrogen content (expressed in wt.% of H in the material): MgH_2 (7.6%) and hydrides of Mg alloys (e.g., Mg_2NiH_4, 3.8%) represent in this respect the current optimum. However, for their use as storage materials a sufficient amount of heating (ca. 300 °C) is necessary for the desorption of the hydrogen. The disadvantage of the presently known, low- and medium-temperature reversible hydrides are the high costs for the intermetallic alloys suitable for the purpose ($LaNi_5H_6$, $TiFeH_2$), combined with their four to five times lower storage capacity (1.8%) compared with say MgH_2.

Alkali-metal-based aluminum hydrides, $AAlH_4$ (A = Li, Na, K) have been found to have a potential as viable modes for storing hydrogen at moderate temperatures and pressures. These hydrides have been demonstrated to have higher hydrogen storage capacity at moderate temperatures and lower cost than conventional intermetallic hydrides. However, a serious problem with these materials is poor kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Bogdanovic and co-workers [1,2] have recently established that sodium aluminum hydrides, which were earlier considered in actual practice as irreversible with respect to hydrogen absorption/desorption, can be made reversible by doping with Ti. Efforts [3,4] have also been made to improve the hydrogen reversibility of $NaAlH_4$ by ball milling in combination with or without additives. In line with this, considerable interest is attached to the structural properties of the series ABH_4 and A_3BH_6 (A = alkali metal; B = B, Al, Ga) at ambient and higher pressures. In this article, we will demonstrate how density-functional theory (DFT) is used to predict unknown crystal structures, chem-

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ical bond characteristics, and high-pressure behavior of hydrides.

In the first part of the paper, we present the structural calculations for some complex hydrides. In the second part, we will consider the chemical bonding in selected hydrides with the help of partial density of states (DOS), crystal-orbital Hamilton population (COHP), charge density, charge difference, electron-localization function (ELF), and Mulliken population analysis. The third part deals with the structural stability of materials at high pressures based on total-energy studies.

2. Computational details

To predict the ground-state structure of Li_3AlH_6 and $KAlH_4$, we have used DFT [5] within the generalized-gradient approximation (GGA) [6], as implemented with a plane-wave basis in the Vienna ab initio simulations package (VASP) [7]. Results are obtained using projector-augmented plane-wave (PAW) [8] potentials provided with the VASP. The atoms are relaxed toward equilibrium until the Hellmann–Feynman forces are less than 10^{-3} eV/Å. Brillouin zone integration are performed with a Gaussian broadening of 0.1 eV during all relaxations. All calculations are performed with 512 and 600 **k** points for Li_3AlH_6 (Mg_3TeO_6-type structure) and $KAlH_4$ ($KGaH_4$-type structure), respectively, in the whole Brillouin zone with 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 [9–12] to reproduce structural properties of ambient- and high-pressure phases. The COHP is evaluated using the TBLMTO-47 package [13]. The Mulliken population analyses were made with the help of the CRYSTAL03 code in which we used 5-11G, 6-11G, 85-11G, and 86-511G basis sets for H, Li, Al, and K, respectively [14].

3. Structural prediction

Prediction and understanding of properties of materials (encompassing even not yet synthesized phases) by theoretical means is a valuable complement to the traditional experimental approach. Theoretical simulation of material properties before preparation and testing may save time, manpower, running costs, etc. Owing to the low X-ray scattering power of hydrogen, poor crystallinity, and the usual structural complexity of hydrides, these structures are often less characterized than other solids. For instance, this is the case for the (assumed technologically interesting materials) alkali boron, alkali aluminum and alkali gallium tetrahydrides, among which only a few is structurally well characterized. In the present section, we are going to show how DFT calculations can be used to predict the structures of the experimentally characterized Li_3AlH_6 (Fig. 1) and uncharacterized $KAlH_4$ compounds.

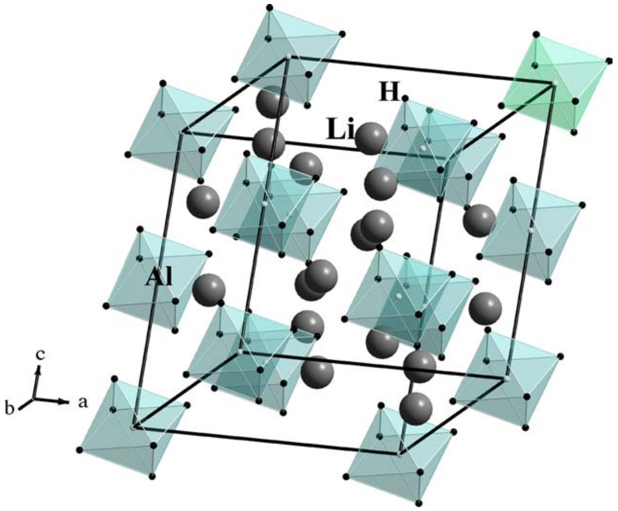

Fig. 1. The Mg_3TeO_6-type crystal structure of α-Li_3AlH_6. Locations of H and Li are shown (and labeled) in the illustration. Al is located at the center of the octahedra.

3.1. *The crystal structure of* Li_3AlH_6

The crystal structure of Li_3AlH_6 has up to recently not been completely revealed and several structure models have been proposed with possible monoclinic ($P2_1/c$, $P2_1/m$, $C2/m$, Cm, or $C2$) and rhombohedral ($R3$, $R3$, $R3m$, or $R3m$) space groups [15–17]. There has been no theoretical attempt to explore the crystal and electronic structures of this compound. However, a fresh experimental study by Brinks and Hauback [18] with combined synchrotron X-ray and neutron diffraction has shown that Li_3AlH_6 crystallizes in space group $R\bar{3}$.

Twenty-one closely related potential structure types were considered for the theoretical simulation. The involved structure types are: Li_3AlF_6, B_3BiO_6, Na_3AlH_6, Na_3AlF_6, Na_3CrCl_6, Mg_3TeO_6, K_3MoF_6, K_3TlF_6, Fe_3BO_6, Cu_3TeO_6, Cu_3WO_6, Rb_3TlF_6, Nb_3BaO_6, Nb_3VS_6, I_3AsF_6, Hg_3SO_6, Hg_3NbF_6, Hg_3TeO_6, Pb_3SO_6, Er_3GaS_6, and U_3ScS_6 [19]. The calculated total energy versus cell-volume curves for the 14 most relevant structural arrangements (the others fall at higher total energy) are shown in Fig. 2. Among them the Mg_3TeO_6-type arrangement (hereafter designated α-Li_3AlH_6; Fig. 2 and Table 1) is found to lead to the lowest total energy, consistent with the recent experimental findings [18]. The calculated unit-cell dimensions and positional parameters at 0 K and ambient pressure are in good agreement with the room-temperature experimental findings [the calculated *a* is within 0.3% of the experimental value whereas the slight underestimation (0.6%) in *c* is typical for the agreement obtained by DFT calculations]. It is interesting to note that the β (Cu_3TeO_6-type) and γ-(Li_3AlF_6-type) modifications

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