Electronic structure of ternary hydrides based on light elements

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Abstract

Ternary hydrides based on light elements are interesting owing to the high available energy density. In this work we focused into the electronic structure of a series of known systems having the general formula AMH_4 (A = Li, Na, M = B, Al). We computed the energy bands and the total and partial density of states using the linear-augmented plane waves method. In this report, we discuss the chemical bonding in this series of complex hydrides.
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1. Introduction

Ternary hydrides based on alkali metals and elements belonging to the IIIB family have deserved an increasing interest owing to the recent demonstrated capability, at least for some of them, to perform reversible decomposition reactions. Since the discovery of this behavior on 1997 by Bogdanovic and coworkers [1], a new possible method for hydrogen storage has been largely investigated. The main interest in using hydrides composed by light atomic mass elements is to increase the hydrogen to total mass ratio yielding an increased value for the specific energy. This figure of merit is crucial for any application involving hydrogen transport. One of the hydride series belonging to this class of compounds exhibit the general formula AMH_4, where A is an alkali metal and M can be B, Al or Ga. In spite of the chemical formula, the AMH_4 hydrides show different crystal structures. It must be noted that a precise crystal characterization of this kind of hydrides demand very accurate diffraction studies on samples of extremely good quality. Unfortunately, this crystal information is not available for all cases. Moreover, the corresponding phase diagrams are frequently fairly known. This family of compounds belongs to a wider class of ternary hydrides exhibiting both, ionic and covalent bonding in the same compound. As it has been largely described in the literature, this situation permit to this family of hydrides to show insulating as well as conducting properties. In the other hand, the stability of these solids are sensible to the extend of covalency between the M-element and the H atom [2].

Starting with the best crystal information available, we investigated the electronic structure of AMH_4 (A = Li, Na, M = B, Al) series of compounds. In the following section we describe briefly some technical details of the energy band structure method. Then, we present and discuss the results obtained for this family of hydrides. We close this report summarizing our must important findings.

2. Methodology

Solid-state electronic structure calculations were carried out using a density functional theory (DFT) approach to band theory, employing the full potential-linear augmented plane

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waves method [3] (WIEN code). The total density of states (DOS) as well as the angular momentum resolved density of states (PDOS) at each atomic site were computed. The exchange part of the crystal potential was modeled by means of the generalized gradient approximation [4] to the local spin density. We selected up to 150 k-points of the irreducible wedges of the corresponding Brillouin zones. For this set of points, we computed the ab initio energy eigenvalues. All the calculations were performed self-consistently and semi-relativistic. The spin-orbit interactions, not relevant in the present cases, were neglected in all the solid state calculations.

3. Results and discussion

We start describing the electronic structure features of the face-centered cubic ($\bar{F43}$ m) hydride $NaBH_4$ because it shows the essential characteristics of the BH_4 unit. In this crystal, the BH_4 specie form a perfect tetrahedra, randomly oriented in the structure. In such a way, two crystallographic sites are half occupied by hydrogen atoms [5,6]. The B–H distances are small (1.17 Å) while the B–B distances are large (4.34 Å). We perform a band structure calculation by considering one of the hydrogen sites fully occupied while the other was kept empty. This yield an ordered structure and we expect that the main characteristics of this hypothetical (ordered) crystal do not differ fundamentally from that exhibited by the true disordered solid. In Fig. 1 we show the total DOS for this f.c.c. hydride. The first structure of the DOS plots, at the bottom of the energy scale, is of a_1 symmetry (at Γ-point, T_d symmetry). The main bonding orbital contributions concern

the B-s, H-s and Na-s orbitals. This structure is filled with two electrons and show a narrow band width (1 eV). At higher energies, a manifold composed of two structures is visible in the DOS plot. The corresponding bands (not shown) are triply degenerate (t_2) at the center of the Brillouin zone and split into two branches; one, singly degenerate, centered at -1.9 eV (of b_2 symmetry at X-point, D_{2d}), and a second one doubly degenerate (e at X-point) and centered at -0.3 eV, responsible of the peak in the DOS plot close to the top of the valence band. These structures are filled with two and four electrons, respectively and result from the B-p/H-s/Na-p bonding orbital interactions. An direct energy band (6.6 eV) separates the valence band from the first unoccupied states. At Γ-point, the first unoccupied states are essentially of anti-bonding nature constituted by B-s orbital with non negligible contributions of Na-s and H-s.

With this simple considerations we can afford the description of the electronic structure of the other hydrides. These compounds are characterized by distorted MH_4 unit, exhibiting different orientations respect to the cationic A^+ sub-lattice.

The $LiBH_4$ hydride is particularly interesting looking for applications because it is chemically constituted by two light elements. The high temperature phase of $LiBH_4$ hydrides is hexagonal (P6$_3$ mc) with two chemical formula-units per cell [7,8]. The band structure is thus formed by eight filled bands well separated from the conduction band (Fig. 2). The energy gap is very high (≈ -6.6 eV) clearly indicating the insulating behavior of this colorless hydride. The analysis of the wave function coefficients at the center of the Brillouin zone show two low energy lying bands mainly composed by the strongly bonding B-s/$H_{1,2}$/Li-s (a_1 at Γ) orbital interactions
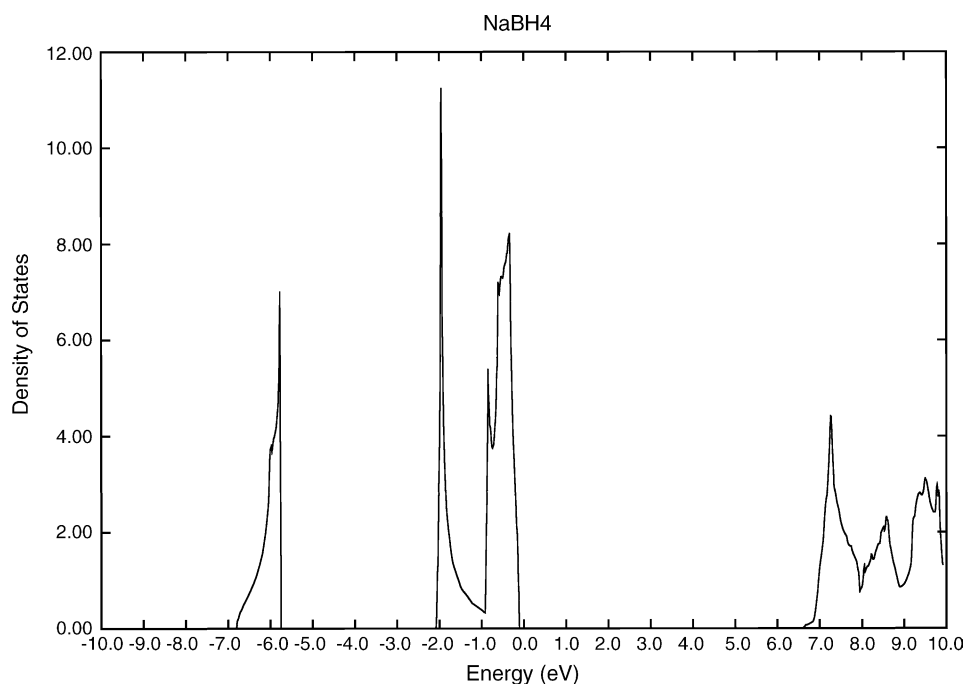

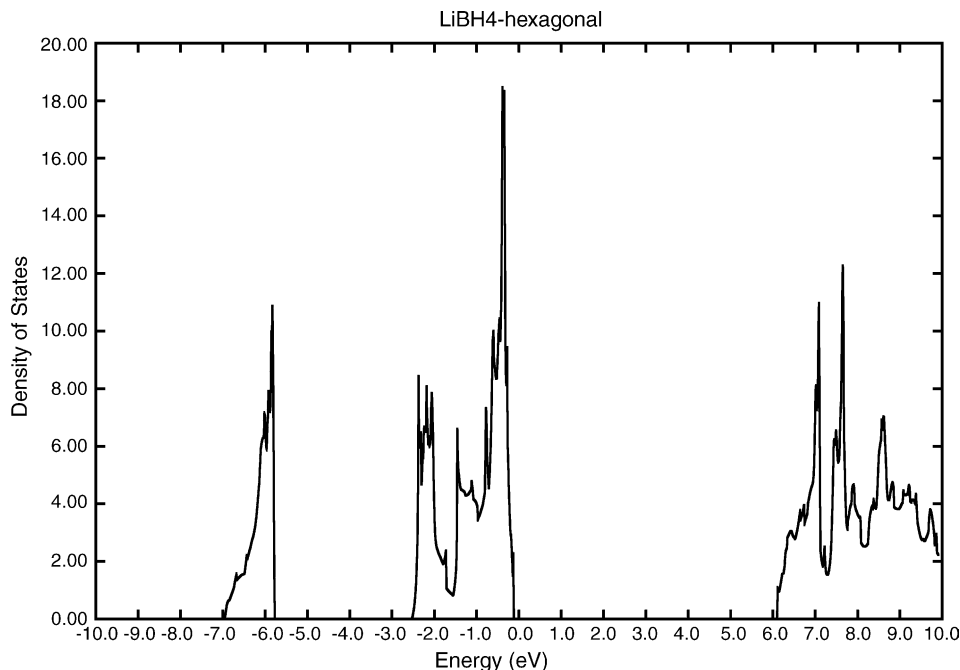Fig. 1. Total density of states (DOS) of the $NaBH_4$. DOS in states of both spins per cell-eV.

Fig. 2. Total density of states (DOS) of the LiBH$_4$ in the high temperature (hexagonal) phase. DOS in states of both spins per cell-eV.

[9]. This reflects a narrow structure (1.20 eV) in the total DOS at around −6.5 eV. At higher energies, we observe two states essentially due to the B-p/H$_1$-s interactions (a$_1$ at Γ) followed by two sets of doubly degenerate states arising from the B-p/H$_2$-s bonding interactions (e$_1$ at Γ). These energy states are associated to both structures appearing from −2.5 eV to the top of the valence band. The charge analysis (integration of the PDOS in the atomic sphere) roughly indicates the charge donor role played by lithium atoms. The first anti-

bonding states appears at the bottom of the conduction band, as indicated, around 7 eV above the top of the valence band. This strong bonding–antibonding splitting is mainly due to the short B–H distances in this hydride (1.27–1.29 Å).

In the other hand, the room temperature orthorhombic (Pnma) phase show 16 filled bands (four unit formula per cell) separated from the conduction band by a 5.9 eV energy gap. This insulating hydride is characterized by a very similar electronic structure to the high temperature variety. A
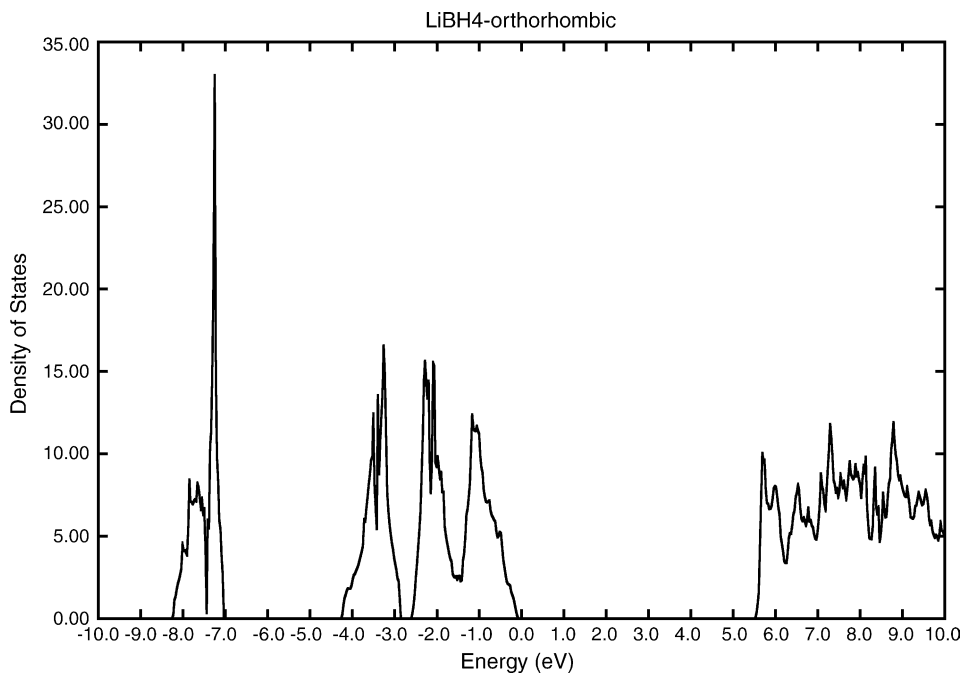

Fig. 3. Total density of states (DOS) of the LiBH$_4$ in the low temperature (orthorhombic) phase. DOS in states of both spins per cell-eV.

low lying block of bands appears at the bottom of the energy scale, yielding a first structure in the DOS plots (Fig. 3). This is composed by the bonding interactions of the B-s/H-s/Li-s orbitals (a_g at Γ), where H_1-s is the major contribution. At higher energies, a second structure is evident in the DOS plot which results from the $H_{1,2}$-s/B-p/Li-p/H_3-s contributions (essentially (b_{2u} at Γ)). Two merged structures complete the valence band involving the B-p/$H_{1,2}$-s/Li-p (essentially b_{3u} at Γ) and B-p/H_3-s/Li-p (b_{1u} at Γ) orbital interactions.

One of the must important differences between both structures is the distortion of the BH_4 unit in the low temperature phase respect to the high one. In the former, it is remarkable one of the B–H distance being 1.04 Å, a very small figure when compared with rest of the B–H distances (≈ 1.25 Å). In the later, the BH_4 unit is more symmetrical and exhibit larger [BH_4]–[BH_4] distances (4.26 Å) compared to the low temperature phase (3.71 Å). This can explain partially the narrower structures observed in the orthorhombic structure and the shift to lower energies of the first σ-bonding bands, compared to the hexagonal phase.

$LiAlH_4$ crystallizes in the monoclinic $P2_1/c$ structure [10,11]. In this hydride the AlH_4 units are fully distorted with Al–H distances ranging from 1.603 to 1.633 Å. Electronic structure computations have been performed for this compound within the DFT approximation for several surfaces. Both, *true two dimensional* as well as a *slab technique* were used in both, the pure $LiAlH_4$ surface [12] and the Ti doped system [13]. However, to our knowledge, no bulk calculations of the electronic structure has been published. The total DOS plotted in Fig. 4 show two structures at the bottom of the energy scale filled with 32 electrons ($Z = 4$). The first structure results from the Al-s/H-s/Li-s bonding interactions

(a_g at Γ) and it is 2 eV width. At higher energies, the complex manifold Al-p/H-s/Li-s,p complete the valence band. An energy gap of 4.8 eV separates the valence band from the N_a-s unoccupied states.

$NaAlH_4$ is the prototype hydride of these technologically important series of compounds. $NaAlH_4$ adopt a more symmetrical configuration compared to the previous discussed lithium based hydride. This compound shows a bct ($I4_1/a$) [14–16] crystal structure where the AlH_4 units are tetrahedral with 1.626 Å Al–H distances. Electronic structure calculations were performed for the bulk material with the projected-APW method by Vajeeston et al. [15]. They found theoretically that α-$NaAlH_4$ ($I4_1/a$) is more stable than the β-phase (Cmc_21). Moreover, they establish that a phase transition should occur under pressure at 6.43 GPa. The computed total and partial DOS for the α-phase are in good agreement with those reported in the present work. Optimized lattice parameters were also calculated for the α and β-phases by Opalka and Anton [17]. In this research, some hydride dismutation reaction were considered in order to yield some light to the high temperature form of β-Na_3AlH_6, an important intermediate in the decomposition path of $NaAlH_4$.

However, this research is focused to thermochemical considerations, thus the detailed electronic structure was not reported. More recent, Aguayo and Singh [18] performed band structure calculations with the same method used in the present research. The methodological difference is only the introduction of the local density approximation to the exchange potential instead of the generalized gradient approximation employed in the present investigation. They studied the electronic structure nature of this complex hydride along with the AlH_3 and NaH hydrides. Their results of the DOS
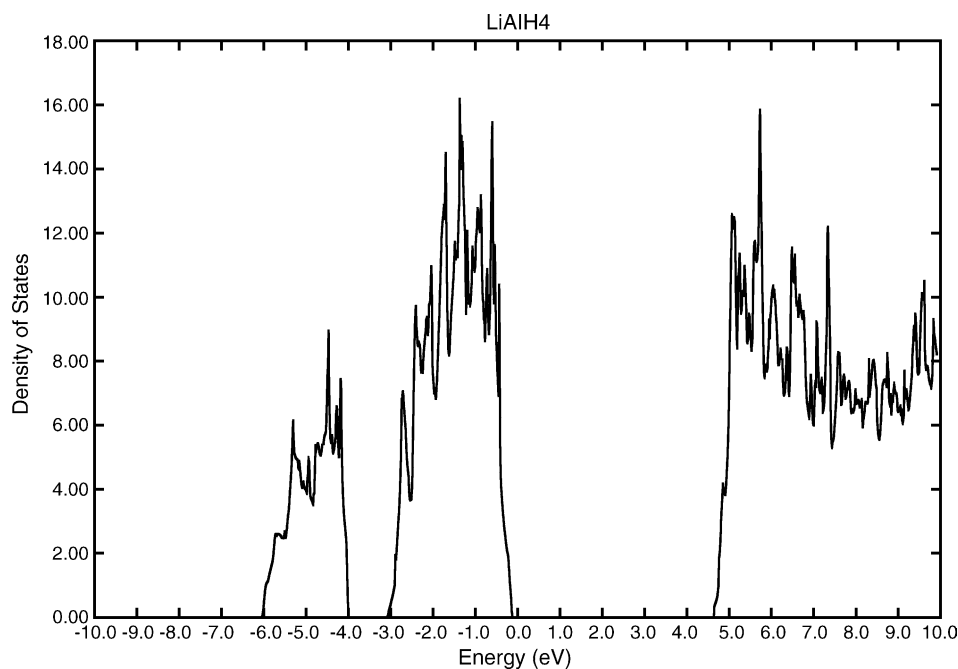

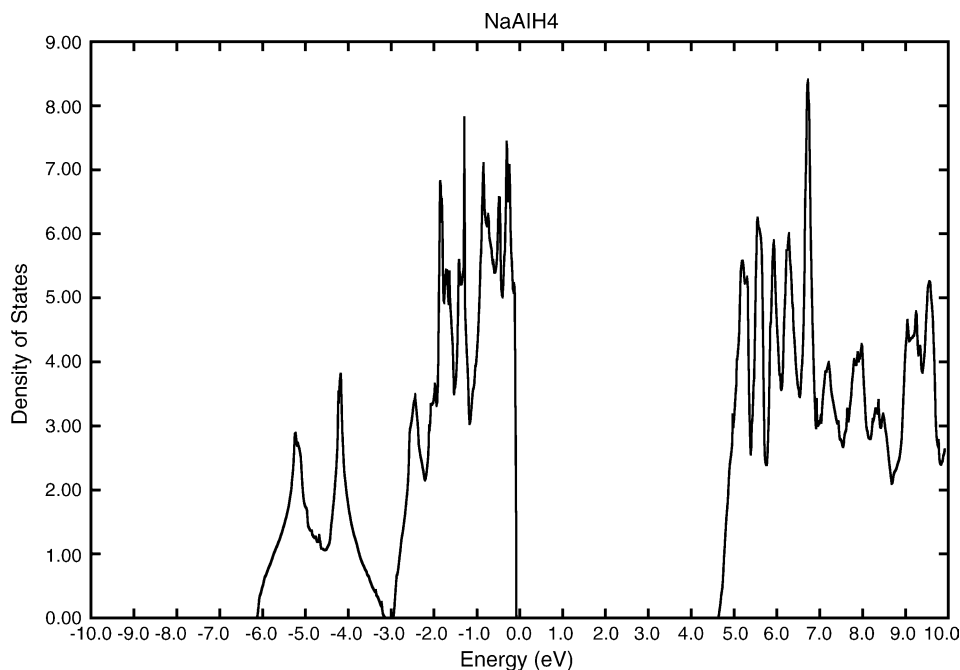Fig. 4. Total density of states (DOS) of the $LiAlH_4$. DOS in states of both spins per cell-eV.

Fig. 5. Total density of states (DOS) of the NaAlH$_4$. DOS in states of both spins per cell-eV.

of NaAlH$_4$ are in good agreement with those obtained in the present investigation. The DOS plotted in Fig. 5 show two structures filled with 16 electrons ($Z = 2$) showing the expected contributions. At the bottom of the energy scale a two peaked structure is obtained from the Al-s/H-s/Na-s and Al-s/H-s (a$_g$ at Γ) orbital contributions, respectively. The following complex structure is essentially composed by the Al-p/H-s/Na-p bonding orbitals (a$_u$ and e$_u$ at Γ). This hydrides shows an energy gap of 4.7 eV separating the valence band from the Al-s/Na-s antibonding unoccupied states.

4. Conclusions

We have investigated the electronic properties of the AMH$_4$ (A = Li, Na, M = B, Al) series of ternary hydrides. We found that these hydrides are insulators with a large energy gap. The main characteristics of the bonding are controlled by the nature of the MH$_4^-$ sub-lattice. Preliminary total energy calculations for the hypothetical reaction A$^+$ + MH$_4^-$ $\longrightarrow$ AMH$_4$ suggest that the electrostatic contributions to the sub-lattices interactions can be as large as 8 eV. We are investigating now the correlation between the sub-lattice interaction energy and crystal details as coordination numbers and interatomic distances.

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