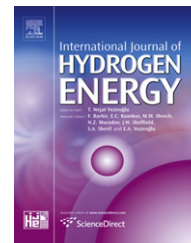


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Technical Communication

First-principles studies of lithium hydride series for hydrogen storage

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ABSTRACT

The application of hydrogen as a clean energy source is based on storage of hydrogen. In metal hydrides is possible, since many metals react readily with hydrogen forming a stable metal hydride. Thus, saline hydrides such as lithium hydride have appeared as new alternatives to this, because of their high reactivity and reversibility. The first principles calculations based on density functional theory (DFT) have been used to study the physical properties of several Li–H compounds. The crystal structure, electronic properties and internal optimization parameters are treated by the LAPW method implemented in the WIEN2k code. In the present study we show the comparison of three different phases of lithium hydride compounds, in six different crystal structures, with the purpose of comparing the formation energies in all cases, and determine which is the structure, with the best structural properties for applications as hydrogen reservoir. The comparisons between the results obtained in the structures of lithium–hydride are discussed in this work. Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The energy sources currently in use (fossil fuels, nuclear energy) have negative impact on the environment, producing irreversible drawbacks.

The development of an appropriate technology to collect a primary energy directly from its source, store it and transport it, has been a problem.

In this sense, hydrogen is known as the fuel of the future, serving as an appropriate energy carrier for current global conditions. Thus, the storage and transport of energy would be made more efficient by utilizing hydrogen [1].

The main advantage of metal hydrides in respect to any other storage medium has been the density of hydrogen.

Safety can be considered another advantage related to metal hydrides [2].

Hydrogen storage in metal hydrides is the safest method, because they operate at relatively low pressures. For this reason, the hydrogen absorption in materials is considered very important.

In many metals, it can lead to premature failure under stress, a phenomena referred to as hydrogen embrittlement (process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen). Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations. This process is believed to be different depending on whether or not stable

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hydrides can be formed. Metal hydrides appear to be the alternative devices of hydrogen storage, because of their good reversibility and their large reactivity [3,4].

Some metals interact with the H to form stable alkaline hydrides. With this consideration, it is necessary to find new compounds that are not as stable, and in this way, hydrogen can easily be released without excessive heating. The

understanding of the basic material properties of metal hydrides is of great interest in improving performance, since the stability of metal hydrides is key to rationally investigate and design potential hydrogen-storage materials [5]. Many attempts have been made to enhance the reversibility of the hydriding/dehydriding reactions and we are motivated to help in the proper selection of the metal hydrides.

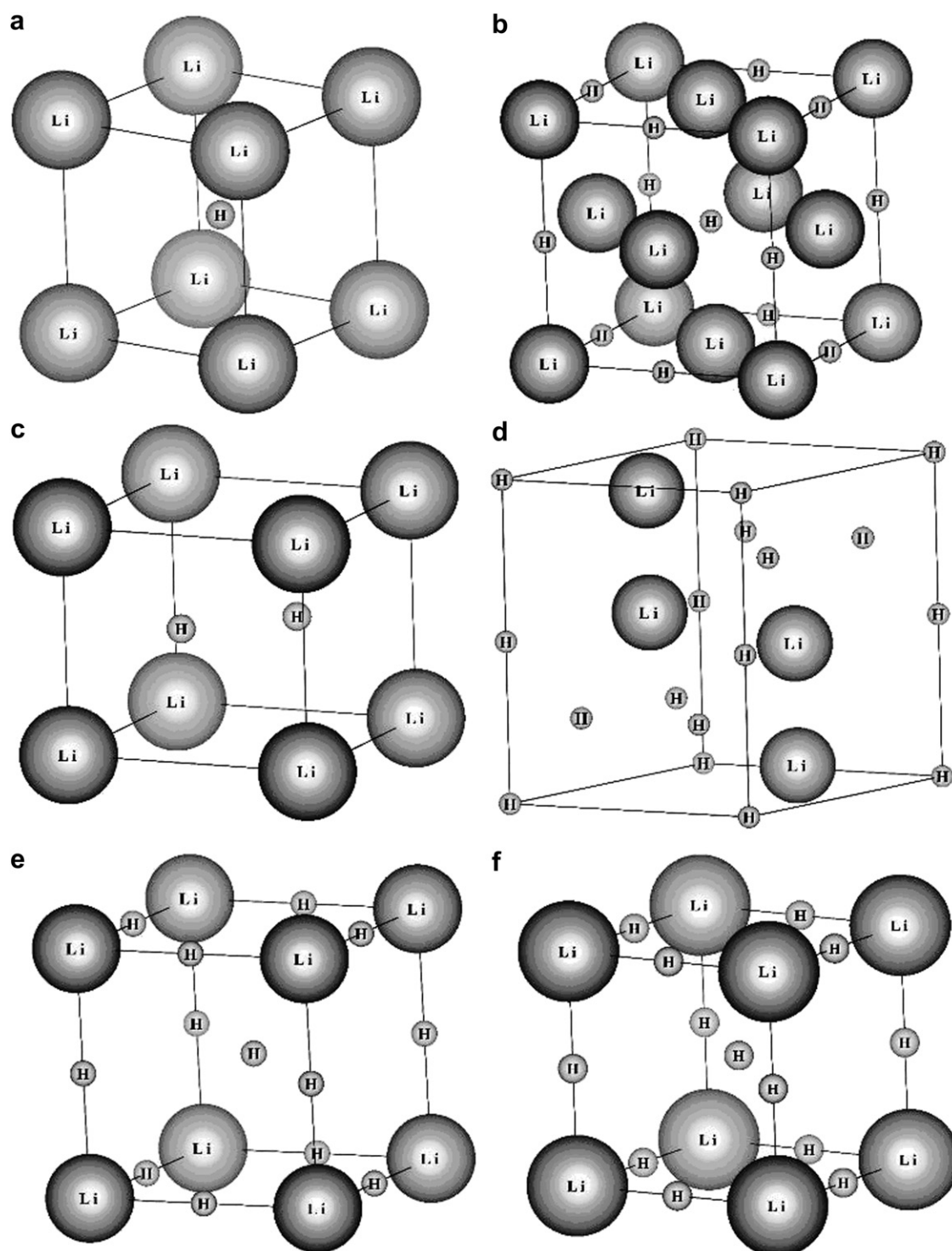


Fig. 1 – Crystal structures of: (a) LiH_{221} and (b) LiH_{225} in cubic phase, (c) LiH_2_{191} and (d) LiH_2_{194} in hexagonal phase, (e) LiH_4_{215} and (f) LiH_4_{221} in cubic phase. Large and small spheres represent Li and H atoms, respectively.

The fundamental objective of this work is to obtain the optimized minimum energies of the lithium hydride compounds studied in order to determine the stability of lithium hydride series and discover additional compounds as alternatives to be utilized in applications for hydrogen storage [6].

2. Method of calculation

The first principles calculations were performed using LAPW method within the framework of density functional theory (DFT) [7] as implemented in the Wien2K code [8,9]. In this way, the exchange-correlation potential for structural and electronic properties was calculated using both a local density approximation (LDA) and the Perdew–Burke–Ernzerhof (GGA) expression [10].

The following parameters were used: (a) $R_{MT} \cdot K_{max} = 7.0$, for LiH_221, LiH_225, LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221, which determines the matrix size, where R_{MT} denotes muffin-tin radii and K_{max} gives the magnitude of the largest K vector in the plane-wave expansion, (b) The R_{MT} of Li and H were: Li (1.74), H (0.94) respectively, (c) for all structures a mesh with 200 k -points was taken in the irreducible wedge of the Brillouin zone.

We have performed six calculations, divided in two structures with different symmetry groups. The description of the different cases are: (a) LiH_225 [11,12], with space group $N^\circ 225$ Fm-3m, NaCl-type structure with Li at (0, 0, 0) and H at (0.5, 0.5, 0.5) and an experimental lattice parameter of 4.083 Å (b) LiH_221 having a cubic structure (space group $N^\circ 221$, Pm-3m) with Li at (0, 0, 0) and H at (0.5, 0.5, 0.5). (c) LiH_2_191 having a hexagonal structure (space group $N^\circ 191$, P6/mmm), with Li at (0, 0, 0) and H at (0.333, 0.666, 0.5) and (0.666, 0.333, 0.5). (d) LiH_2_194 also having a hexagonal structure (space group $N^\circ 194$, P6_3/mmc), with Li at (0.333, 0.666, 0.062) and H_1 (0, 0, 0) and H_2 (0.83, 0.667, 0.25) (e) LiH_4_215 having a cubic structure (space group $N^\circ 215$, P-43m) with Li at (0, 0, 0) and H at (0.333, 0.333, 0.333). (f) LiH_4_221 having a cubic structure (space group $N^\circ 221$, Pm-3m) with Li at (0.0, 0.0, 0.0) and H at (0.5, 0.0, 0.0) and (0.5, 0.5, 0.5).

3. Results and discussions

3.1. Structural properties

We have proposed the theoretical study of six crystal structures, one of them being LiH_225 with known experimental data. For this compound, we have compared the values obtained with the experimental ones. The five remaining structures have been developed theoretically as potential structures to hydrogen storage. LiH_221, LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221 have not yet been synthesized, and there are no references on experimental studies, different from 225 cubic phase. The six structures have been developed theoretically.

For structural properties, we must know the energy, as well as the crystal structure of the crystalline phases LiH_n , $n = 1, 2, 4$. Fig. 1 illustrates the six crystal structures with those carried out in our theoretical calculations.

The static properties as lattice equilibrium constant (equilibrium volume V_0), bulk modulus and ground state

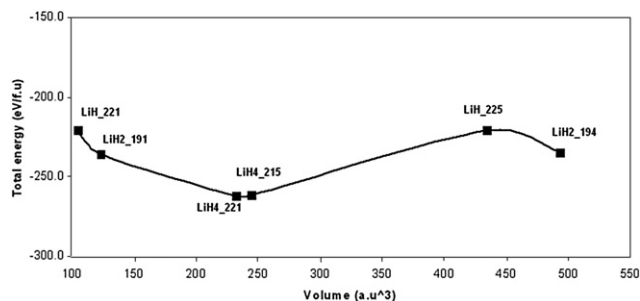


Fig. 2 – Total energy (eV/f.u.) vs unit-cell volume for: LiH_221, LiH_225, LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221.

energy E_0 were obtained from the total energy and fitted with the Murnaghan equation [13,14].

One of the important facts that we want to determine are the different total energies that indicate directly the stability of the compound. According to these values we will be able to determine the degree of the stability of the different compounds. In Fig. 2 we have showed the total energy for the equilibrium values. Each of these points was obtained by the fit mentioned before.

The calculated equilibrium parameters are given in Table 1.

3.2. Electronic properties

The electronic structure of a material contains important information about the characteristics of the materials; it is necessary to determine whether the material is a metal, semiconductor or an insulator.

Fig. 3(a–f) represents the electronic densities of states (DOS) as a function of energy. We cannot be sure, due to limits of the theoretical calculations performed in the frame of DFT, of the value of the band gap, but what we can say is that some of the compounds are insulators (Fig. 3(a–b)). For the LiH_225; we observe a wide band above the Fermi level. The broadband in LiH_225 arises from the equivalence of the Li 2s and hydrogen 1s orbital in energy and geometry, allowing for a significant hybridization [15].

Fig. 3 (c–f) for LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221 structures have metallic behavior.

Table 1 – Optimized structural parameters of lithium series.

Hydrides	Phase	Space group	Volume		Energy eV/f.u
			a.u. ³	a.u. ³	
			Cal.	Exp.	
LiH	Cubic	221	105.2	453.6[12]	-220.9
		225	434.9 ^a		-221.4
			431.2[12] ^b		
LiH ₂	Hexagonal	191	124.2		-235.8
		194	493.9		-235.0
LiH ₄	Cubic	215	245.5		-261.5
		221	232.9		-262.2

a In the present work.

b Calculations performed with the VASP code.

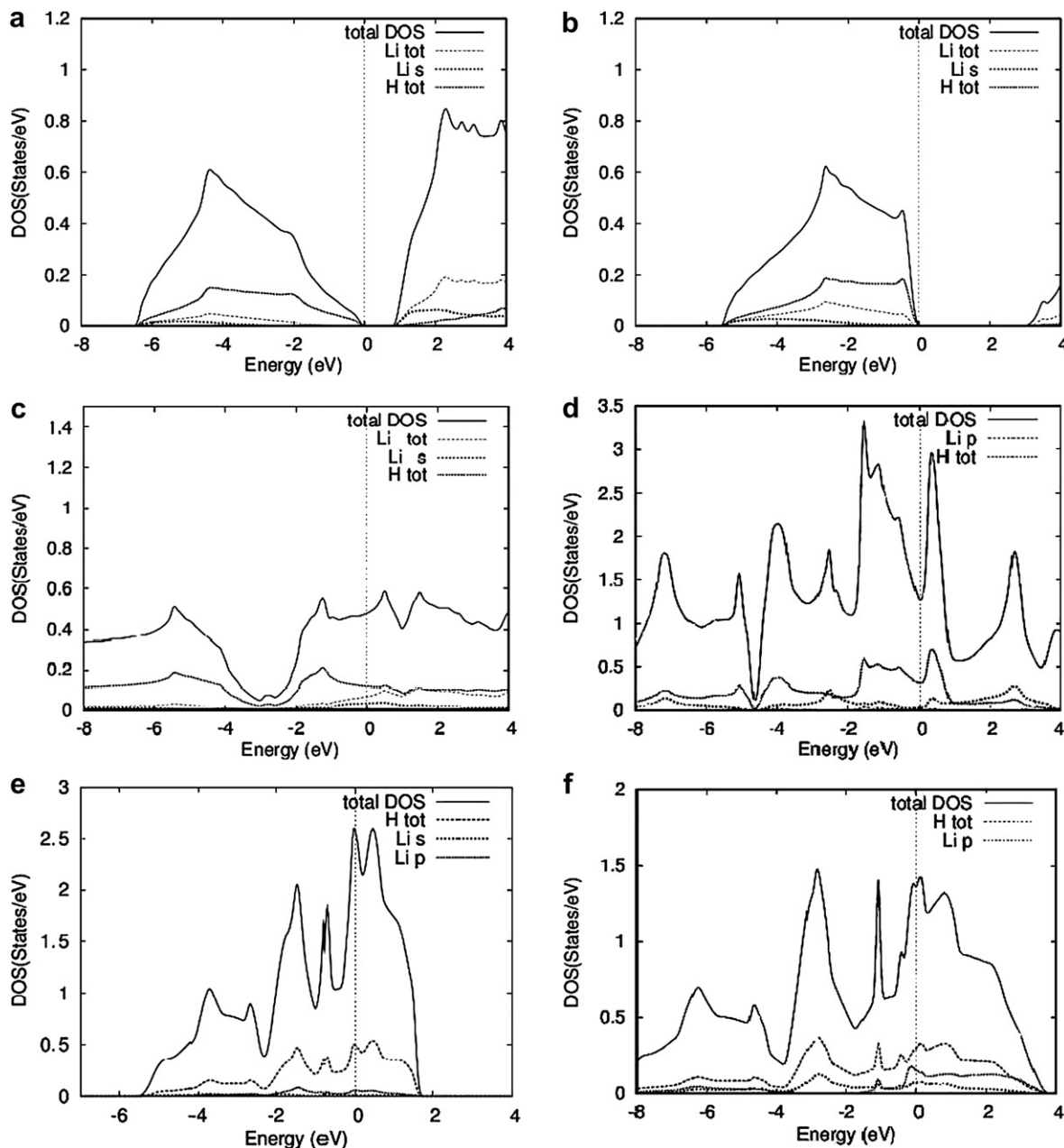


Fig. 3 – Calculated DOS for: (a) LiH_221, (b) LiH_225, (c) LiH2_191 and (d) LiH2_194 (e) LiH4_215 (f) LiH4_221.

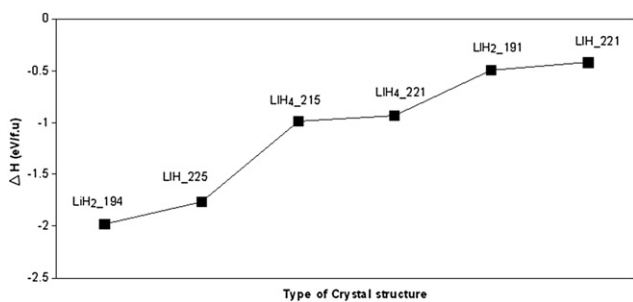


Fig. 4 – Average enthalpy for all structures.

The zero of energy at the Fermi level has been represented with a dotted line, while the contribution of the Li and H atoms to metal-hydrogen bonding can be observed.

3.3. Energy of formation. Enthalpy

In order to study the phase stability of saline hydrides, which is necessary to calculate the energy of formation and is one of the most important quantities for hydrogen storage systems, the conditions of hydrogenation and dehydrogenation depend strongly on the energy of formation in the design of materials for hydrogen storage. Hydrogenation affects the host metal lattice and induces various effects such as lattice expansion and structural transformation [16].

Table 2 – Comparison of calculated enthalpies.

Hydride	Space group	ΔH [eV/H ₂]	
		VASP [18]	Wien2k ^a
LiH	225	–1.80	–1.76
a Present work.			

The energy of formation ΔH may be decomposed into the following terms: $E_{\text{transform}}$, is the energy required, to transform the host metal lattice into the arrangement of the metal ions in the metal hydride, $E_{\text{expansion}}$, is the energy required to expand the host metal lattice to that of the hydride and finally E_{hydride} , is the hydrogen insertion energy in the expanded metal lattice (sic) Andreassen et al. [17]. (ΔH_f in this work is represented as ΔH).

$$\Delta H_f = E_{\text{transform}} + E_{\text{expansion}} + E_{\text{hydride}} \quad (1)$$

The hydrogen absorption process is exothermic ($\Delta H < 0$). The more exothermic the reaction, the more negative the enthalpy, according to the reaction:



Where M stands for the metal, H₂ hydrogen molecule and MH_x the metal hydride formed, x denotes the molar ratio of hydrogen to metal.

The hydriding process is described in Fig. 4, which shows the maximum absorption hydrogen in each structure and the appearance of the other phases studied in this work.

From Fig. 4, we can observe the average values of enthalpy calculated for all structures, showing clearly that, LiH₂_194 is a metallic structure very stable (has a high cohesive energy), the stretching of the metal–metal bonds, necessary for hydride formation, comes at the high energy cost. In consequence, the hydride formation energy is lower.

From Table 2, the results of Wolverton et al. [18] in this work, they performed calculations of energy of formation at LiH, which was –87 KJ/mol H. W. Grochala et al. [19] also performed studies on energy of formation, experimentally at LiH obtained –116 KJ/mol H (1 eV/H₂ = 96, 48 kJ/mol H₂). We also compared the energies of formation calculated at LiH_225, which have approximately ~ 2% of precision between the results obtained for VASP and WIEN2k code. In comparison with the experimental data, the theoretical results are ~ 0, 6 eV/H₂ higher than the experimental.

4. Conclusions

We have examined the stability of LiH_n (n = 1, 2, 4) for LiH_221, LiH_225, LiH₂_191, LiH₂_194, LiH₄_215 and LiH₄_221 by the first-principles calculation with three different phases to the storage of hydrogen.

For the compound LiH_225, we have compared our results with the experimental ones, obtaining a very good agreement between them.

From the DOS plots, we can observe a higher contribution of H in all structures. The largest contribution to the hydride formation energy is: E_{hydride} also named chemical effect,

which provides the stabilization for the hydride and generally grows more positive (less stabilizing) across all structures studied in this work.

However, from the results of the enthalpies we can make a comparison between the different structures suggested and conclude that the LiH_221 is the best structure which could carry out the storage of hydrogen by using less energy in the chemical process of transformation (exothermic reaction) of the hydrogen. This metal hydride has a great potential for generating in hydriding reactions.

On the other hand, for another structures studied, they would be more difficult and expensive to carry out the extraction of H₂ from these structures, therefore, would not be the most recommended structure for one hydrogen storage system.

For this reason, first-principles calculations offer an excellent way to predict new compounds for hydrogen storage or to obtain information on metal hydrides that is difficult to access experimentally.

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