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First-principle calculation of MgH_2 and LiH for hydrogen storage

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Abstract - *First-principles calculation has been performed on the simple hydrides LiH and MgH_2 using the full-potential linearized augmented waves (FP-LAPW). The electronic structure and structural stability are studied. The formation energy has been investigated on these promising candidates for hydrogen storage applications. Our calculated results generally are in good agreement with experimental data. The differences were discussed in this paper.*

Résumé - *Dans ce travail, nous avons étudié deux simples hydrures LiH et MgH_2 par le calcul du premier principe en utilisant la méthode de linéarisation LAPW. Les structures électroniques et cristallines d'équilibre ont été étudiées, ainsi que l'énergie de formation de ces deux hydrures prometteurs dans les applications de stockage solide d'hydrogène. Nos résultats du calcul sont confrontés aux données expérimentales.*

Keywords: Hydrides – FP-LAPW - Formation energy – Hydrogen storage.

1. INTRODUCTION

The large scale utilization of hydrogen as a fuel crucially depends on the development of compact storage materials with a high mass content of hydrogen [1].

One of the major problems encountered when utilizing metal hydrides for hydrogen storage is the low hydrogen weight capacity of these compounds. This disadvantage is due to the low atomic mass ratio of hydrogen to most of the metals and alloys. There are, however, certain additional requirements imposed on a hydrogen-storing material, e.g. moderate stability (ability to release hydrogen in the ambient temperature range), fast kinetics of absorption and desorption and resistance towards hydrogenation poisons; these requirements preclude the use of light metals such as lithium or magnesium for hydrogen storage purposes [2].

The ideal hydrogen storage material should have a high gravimetric hydrogen density, which requires the use of light metals. Moreover, the formation energy of such a material has to be such that it is stable at room temperature, yet it has to decompose at low temperature to release its hydrogen. In principle a large variety of hydride (ex: alanates and boranates) can be synthesized by changing the metal cations, which can be used to tune the formation energy [3].

Since synthesis is a very time consuming effort, there is a need for a materials specific theory with a predictive power for the Formation Energy (FE). At present the state of the art is formed by first principles calculations based upon Density Functional Theory (DFT). Several papers have been dedicated to trends in the DFT Fees of hydrides (alanates and boranates [3-7]). There exists a surprising variety of crystal structures among these compounds. In DFT calculations the crystal structure with the lowest energy has to be searched for each compound, and the cell parameters and the atomic positions have to be optimized.

In this work we try to show how the first-principles calculations can be useful to understand the most important properties of hydrides. So we study here two simple hydrides:

a - LiH is the simplest in term of its low molecular weight.

b - MgH_2 one of the most important for the reversible storage of hydrogen because of the high percentage of this element that it can contain (the theoretical hydrogen storage capacity of pure Mg is up to 7.6 % of Hydrogen); also for its light weight and low cost.

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2. COMPUTATIONAL METHODS

The present calculations have been performed using the full-potential linearized augmented plane-wave method (FP-LAPW) [8]. This is an implementation of density functional theory with different possible approximation for the exchange and correlation potential. The Kohn-Sham equations are solved using a basis of linearized plane wave [9]. The generalized gradient approximation (GGA) parameterized by Perdew *and al.* [10] is adopted for the exchange-correlation energy. In all our calculations we have used the tetrahedron method on a grid of 1000 k points in the whole Brillouin zone. Muffin-tin radius of 1.8, 1.7 and 1.1 Bohr are used for Mg, Li and H respectively.

3. STRUCTURAL DETAILS

LiH has a simple rock salt structure. It have a like NaCl-type structure with Li (0, 0, 0) and H (1/2, 1/2, 1/2) and a lattice parameter of 4.083 Å [11]. The hydride MgH_2 crystallized in the tetragonal structure (space group $P4_2/mnm$ N°136) [12]. The Wyckoff position of Mg and H are 2a (0, 0, 0) and 4f (0.304, 0.304, 0) respectively. The lattice constants used as input for our calculation are the experimental values a = 4.501 Å and c = 3.01 Å [12]. Also the lattice constants of hcp Mg and bcc Li are taken from reference [11].

4. RESULT AND DISCUSSION

4.1 Structural optimization

We have optimized the structural parameters for LiH and MgH_2 by fixing the experimental atomic position and varying the cell volume by ± 15, ± 10 and $\pm 5\,\%$ of the experimental volume V_0; and we have calculated total energy versus volume (Fig. 1 and Fig. 2).

We have optimized the MgH_2, structure and calculated the total energy as function of unit cell volume (Fig. 1).

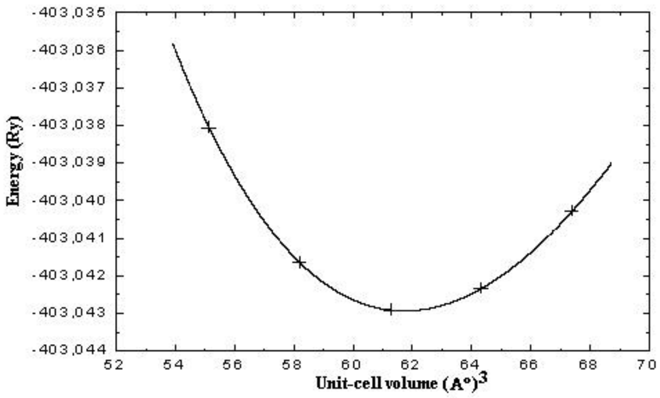

Fig. 1: Calculated free energy versus unit-cell volume for MgH_2

The structure parameters, the bulk modulus B_0 and the pressure derivative $B_0^{'}$ listed in **Table 1** were giving by fitting the total energies to Murnaghan equation of state [13].

Table 1 show that the calculated values are in good agreement with those obtained in previous works [12, 14-16].

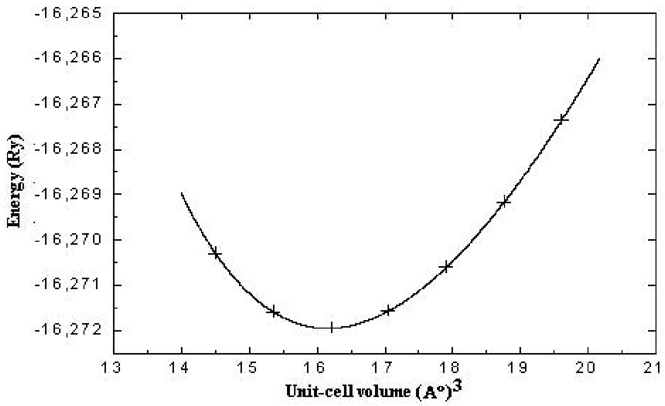

Fig. 2: Calculated free energy versus unit-cell volume for LiH

Table 1: Optimized structural parameters, bulk modulus (B_0) and its pressure derivative (B_0') of MgH_2

a (Å)	c (Å)	B_0 (GPa)	B_0'
4.519	3.022	51.0459	3.5343
4.501 [12]	3.01 [12]	55 [14], 50 [15], 51 [16]	(3,45 [16])

The same procedure was adopted for LiH (Fig. 2) and the **Table 2** gives our results. Our calculated values are in good agreement with the experimental values. DFT and GGA can be used widely to predict the structural and the elastic proprieties of hydrides for hydrogen storage application.

Table 2: Optimized structural parameters, bulk modulus (B_0) and its pressure derivative (B_0') of LiH

a (Å)	B_0 (GPa)	B_0'
4.013	36.0705	3.4952
4.083 [11]	33.6 [17], 34.24 [18]	

4.2 The formation energy (formation heat)

The reaction related to the formation of the hydride MgH_2 is:

$$Mg + H_2 \quad \rightarrow \quad MgH_2 \tag{1}$$

To calculate the formation heat of the reaction (1) we subtracted the total energies of the pure element Mg and the hydrogen molecule from its hydride MgH_2 :

$$\Delta H\,(MgH_2) = \Delta E\,(MgH_2) - \Delta E\,(Mg) - \Delta E\,(H_2) \tag{2}$$

The same idea is used to evaluate the formation energy of LiH via the reaction:

$$Li + \frac{1}{2}H_2 \quad \rightarrow \quad LiH \tag{3}$$

In **Table 3**, we summarized the total energy and the formation enthalpy computed. For MgH_2 and LiH ; we used the total energies obtained with the optimized structure of MgH_2 LiH Mg and Li. The total energy of the hydrogen molecule is - 2.32 Ry [19, 20].

Table 3: Calculated heat of formation of MgH_2 and LiH (f.u: formula unit)

Elements	Total Energy (Ry/f.u)	Formation Heat (kJ/mol H_2)
Mg	-400.6627005	
Li	-15.043991	
H_2	-2.32	
MgH_2	-403.042937	78.946 (-76.15 ± 9.2 [21])
LiH	-16.271951	178.137(162 [22], 167.8 [23], 157 [24])

The calculated heat of formation of MgH_2 is 78.95 kJ/mol. H_2, and is in good agreement with the corresponding measured experimental value 76.15 ± 9.2 kJ/mol. H_2 [21].

Our heat of formation of LiH is acceptable. The discrepancy can be explained by the zero-point energy due to the vibration motion [22]. If we calculate reaction enthalpies from total energy differences only, we neglect the contributions from atomic vibrations. Such contributions are negligible for heavy elements (magnesium), whereas they may be significant for hydrogen and lithium [22].

4.3 Electronic structure

In this section, the lattice parameters were fixed at the calculated values (a = 4.519 Å and c = 3.022 Å). The total and the partial densities of state for MgH_2 are plotted in Fig. 3. There is hybridization between the H and the Mg states in the valence bands which have a dominant hydrogen character.

The electronic structure is non-metallic with the energy gap of 3.60 eV. This value is in excellent agreement with the theoretical findings which reported a band gap around 3.4 eV [14, 15] and close to the value (4.2 eV) calculated by Vajeeston *and al.* [16].

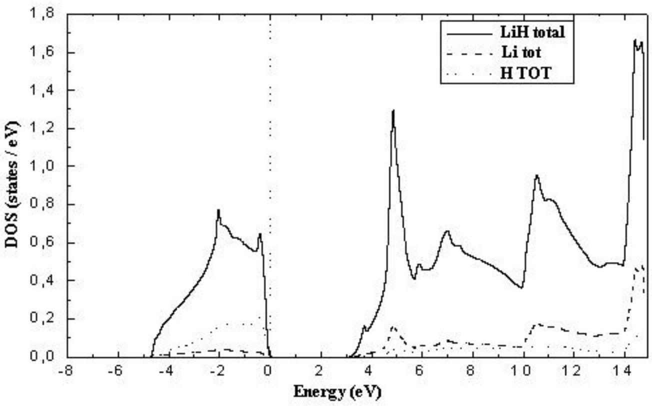

Fig. 3: Total and partial densities of states (DOS) for MgH_2, the Fermi level is set as zero energy and marked by the vertical lines

An experimental UV absorption study gave an absorption edge at 5.16 eV [15]. The divergence between the theoretical and the experimental studies is very clear, it is due to the accuracy obtained by the DFT theory for semiconductors and insulators where the DFT calculations severely underestimate the gap originate from the use of GGA exchange correlation functional [25].

In Fig. 4 we give DOS of LiH : it is non metallic and our calculated band gap is about 3.2 eV and as have been said above, DFT severely underestimate the experimental gap (4.99 eV for LiH at T = 4.2 K [26, 27]).

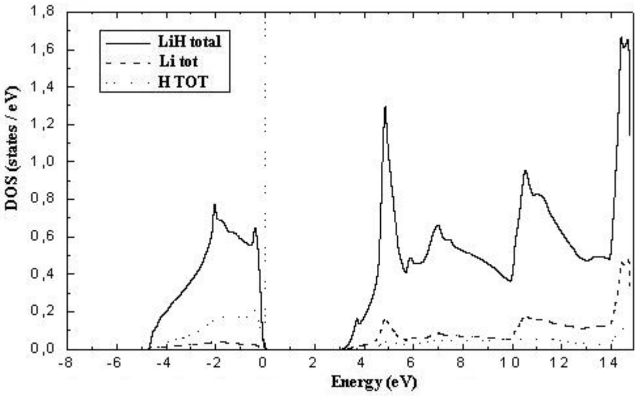

Fig. 3: Total and partial densities of states (DOS) for LiH ,
the Fermi level is set as zero energy and marked by the vertical lines

5. CONCLUSION

In this work the electronic structure of the simplest hydrides LiH and MgH_2 has been studied by the first-principles calculations. The equilibrium structures of these compounds are obtained from DFT/GGA total energy minimization. The enthalpy of formation was calculated theoretically and this quantity is very important to choose the hydrides for hydrogen storage application. The results were close to the experience and we can say that the first principles calculation “is an important tool for modelling materials, hydrides and nanotubes for hydrogen storage applications.

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