



Hydrogen storage in lithium hydride: A theoretical approach

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ABSTRACT

First principles calculations have been carried out to analyze structural stability of lithium hydride (LiH) in NaCl phase using the full potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT). Calculations have been extended to physisorbed H-atom compounds LiH-H₂, LiH-3H₂ and LiH-4H₂. The obtained results are discussed in the paper. The results for LiH are in excellent agreement with earlier reported data. The obtained direct energy band gap of LiH is 3.0 eV which is in excellent agreement with earlier reported theoretical band gap. The electronic band structure plots of the hydrogen adsorbed compounds show metallic behavior. The elastic constants, anisotropy factor, shear modulus, Young's modulus, Poisson's ratio and cohesive energies of all the compounds are calculated. Calculation of the optical spectra such as the real and imaginary parts of dielectric function, optical reflectivity, absorption coefficient, optical conductivity, refractive index, extinction coefficient and electron energy loss are performed for the energy range 0–15 eV. The obtained results for LiH-H₂, LiH-3H₂ and LiH-4H₂, are reported for the first time. This study has been made in search of materials for hydrogen storage. It is concluded that LiH is a promising material for hydrogen storage.

1. Introduction

Hydrogen is considered as a possible substitute for fossil fuels because it is the most copious element in the universe; it is renewable and possesses high substance energy [1]. 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 [2]. The main problem in building a future hydrogen-based energy system is to find out safe methods to store large amount of hydrogen. The global energy demand has increased exponentially and is expected to increase by 75% in the period 2000–2030. In this regard Danish scientist, Poul La Cour (1846–1908) was the first person who gave an idea to create a hydrogen society [3].

The highest volumetric densities of hydrogen are found in metal hydrides. Many metals and alloys are capable of reversibly absorbing large amounts of hydrogen. The group one, two and three light metals (e.g. Li, Mg, B, Al) can combine with hydrogen to form a large variety of metal-hydrogen complexes. These are especially interesting because of their light weight and because of the number of hydrogen atoms per metal atom, which is two in many cases [4,5]. The metal hydrides for hydrogen storage need to be able to form hydrides with a high hydrogen-to-metal mass ratio, but they should not be too stable, so that the

hydrogen can easily be released without excessive heating [6]. The ideal hydrogen storage material should have at least six major criteria: gravimetric capacity, volumetric capacity, kinetics, heat transfer, energy efficiency and reversibility.

On these grounds alkali metal hydride compound, e.g. LiH can be used for hydrogen storage [7]. Sigalas in his recent paper [8] has mentioned that LiH possesses the highest hydrogen content than any other hydride. LiH has also attracted much attention because of their use in nuclear industry [9]. LiH is the simplest alkali hydride, crystallizes in NaCl phase (Space Group No. 225, *Fm-3m*) and its electronic properties have been a subject of wide-range investigation [10–13].

For mobile and stationary applications the volumetric and gravimetric density of hydrogen in a storage material is crucial. Zuettel [4] has mentioned that there are six options for hydrogen storage: (1) high-pressure gas cylinders, (2) liquid hydrogen in cryogenic tanks, (3) adsorbed hydrogen on materials with a large specific surface area (at $T < 100$ K), (4) adsorbed on interstitial sites in a host metal (at ambient pressure and temperature), (5) chemically bonded in covalent and ionic compounds (at ambient pressure), or (6) through oxidation of reactive metals, e.g. Li, Na, Mg, Al, Zn with water. Zurek et al. [14] have mentioned that all of the high LiH phases with unusual stoichiometries (LiH_{*n*}, $n = 2, 6, 8$) become enthalpically stable relative to LiH and H₂.

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There are remarkable structural varieties in the stable LiH_n ; some contain only H_2 units, some both H_2 and H — (or a host LiH lattice with H_2 guests). They have shown that stability range of LiH_2 , LiH_6 and LiH_8 are, respectively, 130–300+, 140–300+ and 100–200 GPa.

Recently Siqi Shi et al. [15] published a paper on Multi-scale computation methods: their applications in lithium-ion battery research and development. They have nicely mentioned that how simulation supplements to experimental efforts in order to bridge experimental and technological gaps. First-principles study of hydrogen storage on graphene with Li atoms by Weiwei Zhou et al. [16] shows that hydrogen storage capacity can be increased to 16 wt % by adjusting the coverage of Li atoms on graphene.

The above mentioned studies motivated us to study hydrogen storage in LiH based on first-principles calculations within the framework of density functional theory (DFT) using the full potential linearized augmented plane wave (FP-LAPW) method as DFT is the most powerful tools for carrying out theoretical studies with high accuracy [17,18]. Therefore, we carried out investigations related to the structural and electronic stabilities of LiH , $\text{LiH}\cdot\text{H}_2$, $\text{LiH}\cdot 3\text{H}_2$ and $\text{LiH}\cdot 4\text{H}_2$ in space group no. 225, $Fm\bar{3}m$ employing DFT and FP-LAPW method. Here our aim is that after adsorption of hydrogen the structure of host LiH will not be change. There is no evidence of previous work for LiH with extra added hydrogen residing in interstitial region at ambient condition. We believe that our results will serve as a good reference data for the application purposes.

2. Computational details

The calculations have been performed using FP-LAPW approach within the framework of DFT as implemented in the Wien2k package [19]. The Kohn-Sham equations are solved using a basis of linearized augmented plane wave [20]. The generalized gradient approximation (GGA) is adopted for the exchange-correlation energy [21]. The dependency of the total energy on the number of k-points in the irreducible wedge of Brillouin zone has been optimized and final size of the k-point mesh is set equal to 10^*10^*10 . A maximum angular momentum for the radial wave function, l_{max} , has been taken as 10 and plane wave cutoff parameter, $R_{\text{MT}}^*K_{\text{MAX}}$ is set equal to 7 for all the compounds, where R_{MT} is the smallest radius of the muffin-tin spheres in unit cell and k_{max} is the magnitude of the largest k-vector in the reciprocal lattice. The iteration process was repeated until the calculated total energy and charge of the crystal converges to less than 0.0001Ry and $0.001e^-$, respectively. The bulk LiH exists in B1 type structure in ground state. The Wyckoff position of atom Li is 2a (0, 0, 0) and that of atom H is 2c (1/2, 1/2, 1/2) [22,23].

3. Results and discussion

3.1. Structural properties

In order to optimize unit cell volume and corresponding total energy of studied compounds, a set of volume versus energy has been obtained using Wien2k and fitted to Murnaghan's equation of state. The exchange and correlation functional is solved using the GGA due to Perdew and Wang [24]. The other equilibrium unit cell parameters are determined by these fits for LiH , $\text{LiH}\cdot\text{H}_2$, $\text{LiH}\cdot 3\text{H}_2$ and $\text{LiH}\cdot 4\text{H}_2$.

Muffin tin radii (R_{MT}) of these atoms play an important role in determining various physical properties [25]. The used values of R_{MT} of constituent atoms and their atomic positions are listed in Table 1. The obtained unit cell crystal structures of LiH , $\text{LiH}\cdot\text{H}_2$, $\text{LiH}\cdot 3\text{H}_2$ and $\text{LiH}\cdot 4\text{H}_2$ are shown in Fig. 1(a)–(d), respectively. In figures Li atoms are shown in green color, basic hydrogen atoms in violet color and extra added hydrogen in red color.

Fig. 1(a) shows unit cell structure of LiH . This unit cell contains $8^*(1/8) + 6^*(1/2) = 4$ atoms of Li and $12^*(1/4) + 1 = 4$ atoms of H. Thus one unit cell contains four formula units of LiH . Fig. 1(b) shows unit cell structure of LiH along with 8 added hydrogen atoms residing inside unit

Table 1

The used values of muffin-tin radius (R_{MT}) and atomic positions of different atoms for LiH , $\text{LiH}\cdot\text{H}_2$, $\text{LiH}\cdot 3\text{H}_2$ and $\text{LiH}\cdot 4\text{H}_2$ in B1 phase.

Compounds	Atom	R_{MT} (a.u.)	Atomic positions
$\text{LiH}\cdot 0\text{H}_2$	Li	1.7	0, 0, 0
	H	1.3	0.5, 0.5, 0.5
	Added H	–	–
$\text{LiH}\cdot\text{H}_2$	Li	1.8	0, 0, 0
	H	1.3	0.5, 0.5, 0.5
	Added H	1.1	0.25, 0.25, 0.75
$\text{LiH}\cdot 3\text{H}_2$	Li	1.9	0, 0, 0
	H	1.3	0.5, 0.5, 0.5
	Added H	1.0	0.00, 0.25, 0.25
$\text{LiH}\cdot 4\text{H}_2$	Li	2.0	0, 0, 0
	H	1.3	0.5, 0.5, 0.5
	Added H	1.1	0.65, 0.35, 0.35

cell exactly in middle of Li-H layer. Distance between two nearest added hydrogen atoms is 2.18 Å. The number of added hydrogen atoms per formula is two (1 hydrogen molecule). Similarly Fig. 1(c) shows unit cell structure of LiH along with 12 added hydrogen atoms residing inside unit cell and $24^*(1/2) = 12$ atoms on surface of unit cell. That is, in this figure, effective number of added H-atoms is 24, meaning thereby six added hydrogen atoms (3 hydrogen molecules) per formula. In this case too, between two adjacent layers of LiH , the added hydrogen atoms form a plane and in one plane 12 hydrogen atoms are arranged in five rows (two on surfaces and three in side unit cell). Also, Fig. 1(d) shows unit cell structure of LiH along with 32 added hydrogen atoms residing, completely, inside unit cell. Between two adjacent layers of Li-H all the hydrogen atoms are arranged in two layers and each layer contains two rows. In this case number of added hydrogen atoms per formula is eight (4 hydrogen molecules).

The obtained equilibrium volume, lattice constant, bulk modulus and first derivative of the bulk modulus in $\text{LiH}\cdot n\text{H}_2$ are summarized in Table 2, along with the available reported data for LiH . From this table it is clear that for LiH our predicted lattice constant 'a' (4.009 Å) is in excellent agreement with the earlier reported theoretical (4.009 Å) [26] and experimental value (4.083 Å) [27]. The obtained bulk modulus 'B₀' (35.76 GPa) is also comparable with its earlier reported value (33.6 GPa) [28]. The results for $\text{LiH}\cdot n\text{H}_2$ ($n = 1, 3, 4$) are reported for the first time.

3.2. Cohesive energy

The total energies of LiH (−16.2719Ry), $\text{LiH}\cdot\text{H}_2$ (−18.3807Ry), $\text{LiH}\cdot 3\text{H}_2$ (−22.6082Ry) and $\text{LiH}\cdot 4\text{H}_2$ (−24.9082Ry) have been optimized. The energy of isolated Li and H atoms are $E_{\text{tot}}(\text{Li}) = -15.04\text{Ry}$ [29] and $E_{\text{tot}}(\text{H}) = -0.97\text{Ry}$ [30]. The cohesive energy of the compounds is defined as:

Cohesive energy = (Energy of free atoms – Crystal energy)

$$E_{\text{coh}}^{\text{LiH}} = (E_{\text{tot}}^{\text{Li}} + E_{\text{tot}}^{\text{H}}) - E_{\text{tot}}^{\text{LiH}} \quad (1)$$

Similarly cohesive energy of the other compounds with 2*n added hydrogen atom are calculated using formula

$$E_{\text{coh}}^{\text{LiH}\cdot n\text{H}_2} = (E_{\text{tot}}^{\text{LiH}} + 2*n * E_{\text{tot}}^{\text{H}}) - E_{\text{tot}}^{\text{LiH}\cdot n\text{H}_2} \quad (2)$$

Thus, by using equation (1) the obtained cohesive energy for LiH (0.2610Ry) is in good agreement with theoretical predicted value, 0.396Ry of N Novakovic [31]. The obtained cohesive energies of other compounds are listed in Table 3.

From the table it is evident that total energy decreases with increase in total number of added hydrogen atoms. The amount of energy released per H-atom during physisorption of two, six and eight H-atoms are respectively, 0.0844 Ry, 0.0860Ry and 0.1095 Ry. It is also evident from the table that cohesive energy of LiH (0.261Ry) is more than the energy released during addition of any single hydrogen atom. Thus to retrieve

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