

# EPJ B

Condensed Matter  
and Complex Systems

EPJ.org  
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Eur. Phys. J. B (2014) 87: 110

DOI: [10.1140/epjb/e2014-40650-3](https://doi.org/10.1140/epjb/e2014-40650-3)

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# Hydrogen reservoirs, an ab-initio study on saline hydrides based on Li/Be-H compounds

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Received 5 July 2013 / Received in final form 17 January 2014

Published online 12 May 2014 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2014

**Abstract.** Research into new materials to be used as hydrogen reservoirs is necessary, the increasing demand of energy in the world should be covered progressively by clean energies, trying not to pollute the environment. With this work we wish to contribute to the knowledge of the different saline hydrides and the possibility of using these as hydrogen reservoirs. We performed a systematic study on these materials. In this work we used different ab-initio codes to study several compounds of lithium and beryllium with hydrogen.

## 1 Introduction

Fossil fuel are the energy sources currently in use, and they have produced a deep and negative impact on the environment, causing irreversible drawbacks, contributing to the greenhouse effect. The big problem to solve is to find new energy sources that replace efficiently the current ones without producing such effects. Generally speaking researchers are looking for one energy generation system whose impact on nature will be as low as possible. One of the biggest candidates for this task is hydrogen (H), which is the most abundant element in the universe, and the lightest in the periodic table. Unfortunately it is very difficult to find it as a free molecule or solid. But it has been shown [1] that by adding some metals, like lithium or beryllium it is possible to have metallic compounds containing H. It is possible to define *energy vectors* [2] as the tools that allow transfer, in space and time, a quantity of energy. In that sense the hydrogen is an energy vector that can be stored, transported and used in many ways.

The critical problem showed for the increasing necessity of, clean and efficient energy, has motivated the research community to move toward issues that have not been developed in the past and they have started to appear in the literature. As hydrogen does not generate the waste produced by fossil fuels, it has been proposed as the fuel of the future, since it is an energy carrier that meets the conditions [1].

One of the challenges in the frame of this problem is to develop appropriate technology to collect this primary energy, store it and transport it. The thermal and electrochemical characteristics of the combustion of H are very favorable. This is one of the challenges of materials sci-

ence today. The use of hydrogen as a source of energy for different applications, as was mentioned in the work of Züttel [3,4], such as: vehicular applications, stationary power generation, etc. The problem is posed, what we are trying to do is to contribute to solving the problem of storing hydrogen, approaching the problem from the standpoint of which are the most suitable materials for this task?

Some metals interact with H in a way that forms stable solid metal hydrides. These compounds have several advantages, one of the top is, that metal hydrides can store a density of H larger than what can be stored as a gas, occupying a smallest volume and with pressures much lower than those required by compressed gas, giving a higher safety factor [5,6].

The absorption of hydrogen in materials is a very important process, giving rise to very different phenomena, such as: a premature failure under stress, which is directly related to the hydrogen embrittlement. This process is believed to be different depending on whether or not stable hydrides can be formed. The metal hydrides show a great advantage and appear to be a great alternative to build hydrogen storage systems, because they have a good reversibility and a high reactivity.

In this work we have obtained, theoretically, electronic properties, total energies, equilibrium volume, density of states, formation energies, etc. of different lithium/beryllium hydride crystal structures. We have studied a restricted number of Li/Be-H compounds, unfortunately only two have been synthesized, in that sense, we are predicting structural parameters, energies of formation and stability of the non-synthesized hypothetical structures.

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The developing of safe and reliable hydrogen storage technology, that improve performance, is critical to the

In our research we have used two different ab-initio codes based on the density functional theory [7,8], the Full Potential Linear Augmented Plane Waves (FPLAW) [9] and more extensively, the Full Potential Local Orbitals (FPLO) [10–12] to realize the theoretical calculations. The reason for this procedure is to obtain the convergence of both methods especially in some of the structures that have not been synthesized yet. Both methods are based on different philosophies and the convergence of them in similar results would show concordance in the values obtained.

We have performed a series of calculations of the two different metal hydrides. The compounds studied were  $M_pH_q$  where  $M$  = metal (Li or Be), with  $p = 1$  to 5 and  $q = 1$  to 7, only in the case of the Li compounds, in the case of the Be-compounds  $p = 1$  and  $q = 1, 2$  and 4. In some cases fixed the values of  $p$  and  $q$ , and we studied the different crystal phases of these compounds.

## 2 Theoretical ab-initio formalism

We have used two different ab-initio codes. One is the full-potential non-orthogonal local-orbital minimum basis scheme FPLO, version: FPLO9.00-34. The non-spin-polarized scalar relativistic DFT total energy and Kohn-Sham band-structure calculations were performed within this scheme. The code is based on a linear combination of overlapping non-orthogonal orbitals with a compact support. The molecular mode of FPLO with free boundary conditions was used. The results reported were obtained using the generalized gradient approximation (GGA) with a parametrized exchange correlation functional according to Perdew, Burke, and Ernzerhof (PBE) [13]. The calculations were carefully converged in numbers of  $k$ -points, regular  $k$ -point meshes were used in the full Brillouin Zone giving never less than 165 in the Irreducible Brillouin Zone (IBZ). The densities were converged down to  $10^{-6}$  for the corresponding parameter in FPLO [ $\text{rms}(\rho_{\text{out}} - \rho_{\text{in}})/\text{uc}$ ].

On the other hand we used, in some cases, the Linear Augmented Plane Wave which is one of the state of the art ab-initio methods within Density Functional Theory. For solving the scalarrelativistic Kohn-Sham equations we have employed the codes implemented in the WIEN2k package [9]. In this method the wave functions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radii  $R_{\text{MT}}$  (muffin tin radius) and in plane waves in the remaining space of the unit cell (the interstitial region). In our calculations we have taken:  $R_{\text{MT}} = 1.55$  a.u. for the Be and  $R_{\text{MT}} = 0.83$  a.u. for the H in the Be-H compounds, while the  $R_{\text{MT}}$  for Li and H in the LiH compounds are 1.74 a.u. and 0.94 a.u., respectively. The maximum  $l$  for the expansion of the wave function in spherical harmonics inside the spheres was taken to be  $l_{\text{max}} = 10$ . The plane wave expansion of the wave function in the interstitial region was truncated at  $k_{\text{max}} = 7.0/\text{min}(R_{\text{MT}})$ , and the charge density was Fourier expanded up to  $G_{\text{max}} = 14$  Ry. The amount of  $k$ -point used depend strongly on the structures studied, we have used meshes of 2000 special  $k$ -points approximately in the whole Brillouin zone, this value is an average of the points used in our calculations. The exchange-correlation functional used was the Perdew-Burke-

Ernzerhof generalized gradient approximation (PBE-GGA) [13]. All the calculations were completely converged to ensure us the best quality of results.

Band structure calculations are a very common tool used to understand some aspects of the electronic structure of materials. Up to now solid state ab-initio researchers have solved the Schrödinger like equations of Hohenberg-Kohn and Sham in the frame of the density functional theory (DFT), using different exchange-correlation energies. In general the accuracy of the results is extremely good, the values of the properties studied differ from the experimental results by very small amounts. This assertion can be seen very easily in the literature. But the exception of this rule is the size of the band gap of insulators and semiconductors. The DFT is a theory of the ground state and is it well known that it always underestimate the value of the band gap. Obtaining the correct band widths has been a wish of researchers for many years. Some time ago, Becke and Johnson [14] based in the Optimize Effective Potential (OEP) method propose a new exchange potential (mBJ) which improve substantially the values of the band gap obtained with other exchange functionals. This potential has been implemented [15] in the Wien2K code [9]. We have used it to obtain the values of the band gap for the compounds, LiH and BeH<sub>2</sub>, the only two that have been studied experimentally.

## 3 Results

Due to the interest that these materials have awakened, we have begun to study their structural properties from the theoretical point of view using first-principles calculations.

Several authors have done calculations of the properties of these compounds [16,17] in the last decade some of them have made first principles calculations [18–22], etc. To obtain many different properties with a high degree of precision.

The self-consistent calculations have allowed us to obtain the density of states (DOS) of each of the compounds and identify whether they are metal, semiconductor or insulator. This information plus crystalline information can be seen in Table 1. It is possible to observe that, in general the Li/Be-H compounds have similar behavior, except in the case of compounds with only one H (MH-221/225). The two series differ here, the LiH compounds are insulator or semiconductor, while BeH compounds are metallic, in both cases the 2nd electron in the 2s orbital of the Be makes its presence felt. When the compounds have more H atoms in the molecule, the participation of this 2nd electron is less noticeable.

We have researched several structures, the two obtained experimentally were the LiH which belongs to the cubic structure NaCl with symmetry group number 225 (Fm-3m), with one formula unit (fu) per unit cell [23], and the other, is the BeH<sub>2</sub> orthorhombic, group number 72 (Ibam), with twelve formula units per unit cell, synthesized for the first time in 1988 [24]. The remaining

**Table 1.** Compounds, formula, phases, groups, number of molecules per unit cell, and type of compound: M = metal, S = semiconductor, I = Insulator.

Meta (M)	Formula	Phase	Space group		Formula unit per unit cell	Type of material	
			Number	Name			
Li	MH <sub>1</sub>	Cubic	221	Pm-3m	1	S	
Be				Pm-3m		1	M
Li			225	Fm-3m	4	I	
Be				Fm-3m		4	M
Li		Tetragonal	129	P4/nmm	2	I	
Li or Be	MH <sub>2</sub>	Hexagonal	191	P6/mmm	1	M	
Li or Be		Hexagonal	194	P63/mmc	4	M	
L		Cubic	224	Pn-3m	2	M	
Li			227	Fd-3m	4	S	
Be		Orthorhombic	72	Ibam	12	I	
Li	MH <sub>4</sub>	Cubic	197	I23	4	M	
Li or Be				215	P-43m	1	M
Li or Be				221	Pm-3m		M
Li	MH <sub>6</sub>					M	
	MH <sub>7</sub>					S	
	M <sub>2</sub> H		224	Pn-3m	2	M	
	M <sub>2</sub> H <sub>3</sub>		221	Pm-3m	1	M	
	M <sub>2</sub> H <sub>6</sub>					M	
	M <sub>3</sub> H <sub>2</sub>					M	
	M <sub>4</sub> H					M	
	M <sub>5</sub> H <sub>3</sub>					M	

structures studied were grouped according the numbers *m* and *n* of metal (M) and H atoms in the formula unit, respectively. All of them are shown in Table 1. To the present, we have no knowledge of previous research that have followed the methodology proposed here.

The first step in our calculations was to determine the structural properties of each compound, minimizing the total energy and obtaining the structural parameters of equilibrium, these values were compared with experimental data, only in the cases of LiH-225 and BeH<sub>2</sub>-72. The equilibrium volume was determined by means of fitting the values of the energy versus volume curves by the Murnaghan equation [25] in the range of  $\pm 10\%$  around the experimental equilibrium volume, when the minimum is known, if not, we used lattice parameters of similar known structures, to start. It is well known that the PBE exchange-correlation potential overestimates the calculated volume parameters, nevertheless, the theoretical values obtained compare very well with the existing experimental values, moreover, the values obtained from the two methods used are almost the same. The values of the equilibrium volume can be seen in Table 2.

We observe, in Table 2, the excellent agreement of both methods with the experimental values of LiH-225 where the difference in volume between experimental and theoretical values is  $-4\%$ , while in the case of BeH<sub>2</sub>-72 the error in the average is  $+7\%$ . The agreement is very good.

As a part of our calculations, we have obtained the pressure of the transition between two different crystal structures for LiH, CsCl (221) and NaCl (225). The values found for the equilibrium volume are in Table 2. From these values can be observed that the equilibrium volume of  $\text{LiH}_{\text{NaCl}}$  is 4 times bigger than the volume of

LiH<sub>CsCl</sub>. According to our calculations, the pressure of the transition is: 330.5 GPa which is very similar to the 329 GPa obtained theoretically [26]. In the theoretical work of Ahuja et al. [19] they also obtain the pressure of the transition using the FPLMTO method, in this case the value of the transition pressure is 400 GPa, in the case of the paper of Hama et al. [27], using the APW method in the frame of the LDA approximation, the pressure obtained was 230 GPa. Wang et al. [28] using the LAPW-PBE, found that the pressure of the transition is 313 GPa. Nowadays the discussion about the value of the pressure is open, as is the discussion about whether the metalization of LiH in the CsCl phase occurs, according to our calculations it is not metallic. According to our knowledge there are no experimental results on this subject in the literature, the theoretical results obtained in reference [29] confirm our results, giving a pressure of transition very similar to that obtained by us. In our calculation we find that the volumes of transition are 100.5 a.u.<sup>3</sup> and 358.4 a.u.<sup>3</sup> for CsCl and NaCl structures, respectively.

Using the advantages provided for the implementation of the mBJ functional in the LAPW code, we have investigated the value of the bandwidth of the LiH-225 (NaCl structure) which has been measured experimentally [29] showing that this compound is an insulator with a gap of 4.99 eV. Also Kondo and Asami [30] measured the energy gap at room temperature, giving a value of  $E_g = 4.94$  eV. Many authors with different methods have obtained values of the energy gap, using GW-GGA [34] a value of

**Table 2.** Equilibrium volumes  $a$  - [23],  $a_1$  - [27],  $a_2$  - [31],  $a_3$  - [26],  $a_4$  - [22],  $b$  - [24],  $b_1$  - [20],  $b_2$  - [32],  $b_3$  - [33].

Hydrides	Phase	Space group	Equilibrium volume (a.u. <sup>3</sup> )			V (a.u. <sup>3</sup> )
			LAPW	FPLO	Exp.	
			Calc.	Calc.		
LiH	Cubic	221		106.8		
		225	433.9	434.9	459.5 <sup>a</sup>	
		225				431.9 <sup>a1</sup>
						403.6 <sup>a2</sup>
						400.3 <sup>a3</sup>
					444.2 <sup>a3</sup>	
					431.1 <sup>a4</sup>	
	Tetrag.	129		250.4		
LiH <sub>2</sub>	Hexag.	191		123.5		
		194		492.6		
	Cubic	221		349.4		
		227		449.9		
LiH <sub>3</sub>	Cubic	197		300.2		
		215		141.1		
		221		141.2		
LiH <sub>4</sub>	Cubic	197		1459.3		
		215		249.4		
		221		233.1		
LiH <sub>6</sub>	Cubic	221				
LiH <sub>7</sub>		221		344.4		
Li <sub>2</sub> H		224		550.1		
Li <sub>2</sub> H <sub>3</sub>		221		270.2		
Li <sub>2</sub> H <sub>6</sub>				576.0		
Li <sub>3</sub> H <sub>2</sub>				378.1		
Li <sub>4</sub> H				502.4		
Li <sub>5</sub> H <sub>3</sub>				651.6		
BeH	Cubic	221		84.1		
		225		315.1		
BeH <sub>2</sub>	Orthor.	72	2079.5	2122.1	1965.1 <sup>b</sup>	
						1 944.7 <sup>b1</sup>
					1926.2 <sup>b2</sup>	
					1934.1 <sup>b3</sup>	
	Hexag.	191		290.1		
194			1266.8			
BeH	Cubic	215		212.1		
		221		185.1		

4.92 eV was obtained, while Kunz and Mickish [35] with a self-consistent Hartree-Fock calculation obtained a value of 6.61 eV, little larger than the experimental one. In references [22,27], the authors made theoretical determinations of the band gap of the LiH (NaCl-structure), the values quoted are 2.93 eV and 4.93 eV, respectively. The calculations of Singh [36] were done at the experimental volume obtaining a direct gap of 5.08 eV at point X in reciprocal space. Our calculation of the band structure was performed after the minimization of the energy volume curves, in the theoretical equilibrium volume, the bandwidth is 5.09 eV and the transition is direct at point X in reciprocal space, agreeing very well with the experimental value.

The present work included the Be-H compounds, we obtained the value of the bandgap  $E_g$  for the BeH<sub>2</sub>-72, taking into account the improvement that uses the mBJ approximation, following the self consistent calculation done to obtain the structural properties. In the

experimental work of Ahart et al. [37] the value of the band gap of the  $\alpha$  phase of crystalline BeH<sub>2</sub> (orthorhombic), was determined to be  $E_g = 5.4$  eV. On the other hand, several authors have calculated the values of the bandgap [26,32,33], where the values obtained were: 5.78 eV, 8.27 eV, 5.51 eV and 5.52 eV, respectively, the first two values belong to the same authors with different methods. These amounts show that this compound is an insulator with approximately 6 eV of forbidden bandwidth. According to our calculations the value of  $E_g$  is 5.58 eV, very close to the experimental value and others theoretical calculations.

In one part of our work involving the study of the structural properties, it is very common that other authors have investigated these properties and this allows us to compare them with the values obtained from our

**Table 3.** Values of  $\Delta E$  for different Li/Be-H compound, 6th and 8th column correspond to Li or Be populations.

Compound	$p$	$q$	$\rho(p+q)$	$\Delta E$ (eV/at.)	Pop. 2s	Pop. H-1s	Pop. 2p
LiH-221	1	1	0.50	-0.169	0.125	1.658	0.198
LiH-225	1	1	0.50	-0.416	0.158	1.570	0.252
LiH-129	1	1	0.50	-0.266	0.128	1.640	0.211
LiH2-191	1	2	0.67	+0.220	0.101	1.352	0.168
LiH2-194	1	2	0.67	+0.509	0.103	1.436	0.203
LiH2-221	1	2	0.67	+0.486	0.213	1.210	0.319
LiH2-224	1	2	0.67	+0.757	0.031	1.355	0.243
LiH2-227	1	2	0.67	+0.644	0.081	1.316	0.308
LiH3-197	1	3	0.75	+0.594	0.053	1.250	0.156
LiH3-215	1	3	0.75	+0.595	0.101	1.217	0.204
LiH3-221	1	3	0.75	+0.597	0.101	1.217	0.204
LiH4-197	1	4	0.80	+0.590	0.088	1.279	0.168
LiH4-215	1	4	0.80	+1.355	0.058	1.150	0.278
LiH4-221	1	4	0.80	+1.214	0.030	1.258	0.229
LiH6-221	1	6	0.857	+0.340	0.090	1.124	0.074
LiH7-221	1	7	0.875	+0.340	0.097	1.095	0.061
Li2H-224	2	1	0.33	+0.019	0.361	1.365	0.423
Li2H3-221	2	3	0.60	+0.144	0.063	1.443	0.294
Li2H6-221	2	6	0.75	+0.609	0.083	1.258	0.314
Li3H2-221	3	2	0.40	+0.118	0.307	1.527	0.308
Li4H-221	4	1	0.20	-0.048	0.435	1.406	0.387
Li5H3-221	5	3	0.375	+0.154	0.189	1.467	0.252
BeH-221	1	1	0.50	+0.996	0.683	1.401	0.778
BeH-225	1	1	0.50	+0.706	0.617	1.323	0.912
BeH2-72	1	2	0.67	-0.011	0.383	1.382	0.855
BeH2-191	1	2	0.67	+0.878	0.553	1.259	0.743
BeH2-194	1	2	0.67	+1.073	0.596	1.333	0.662
BeH4-215	1	4	0.80	+1.037	0.058	1.158	0.276
BeH4-221	1	4	0.80	+0.869	0.272	1.392	0.568

calculations. The bulk modulus is an important physical property and is obtained as a second derivative of the total energy around the energy minimum. When we are comparing the bulk modulus, in fact, we are comparing the quality of the values obtained. The value calculated for the bulk modulus ( $B_0$ ) of LiH-225 (NaCl-structure) was 36.29 GPa very close to 35.7 GPa [38] or 33.9 GPa [39] obtained experimentally. Several authors have published the theoretical values of the bulk modulus ( $B_0$ ), 36.6 GPa [23], 25.5 GPa [40], 33.9 or 36.1 both [34] calculated with GGA but, the first value included the zero point vibrations, while the second value did not. This author, also calculated the Cerperly-Alder parametrization of the LDA exchange-correlation potential and the values were 35.9 GPa and 40 GPa, respectively.

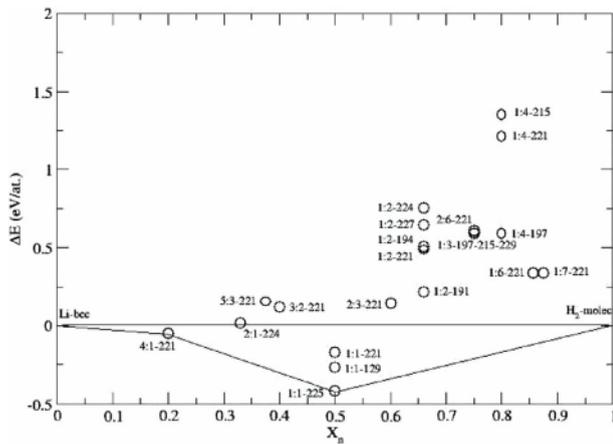
In the case of the BeH<sub>2</sub>, we have no knowledge of experimental measures of the bulk modulus, in the present work we have obtained the value 25.2 GPa, similar to the 24.7 GPa, predicted with the CASTEP package in the work of Hantsch et al. [20]. For these authors, the derivative of  $B_0$  with respect to the pressure ( $B'$ ) is 3.9, while our value is 3.18. The values obtained in reference [32] were 23.79 GPa for  $B$  and 4.24 for  $B'$ . The calculations performed in reference [41] present little difference to the rest of the values shown before,  $B = 21.4$  GPa. In the case of the calculation done by Wang et al. [33] the value for the bulk modulus was 24.19 GPa, the last two

authors do not report values for the pressure derivative of the bulk modulus.

The problem of comparing the energies of the compounds studied here is the amount of the hydrogen atoms existing in the molecule. The comparison is possible when we treat compounds with the same number of atoms of M and H, otherwise it is not possible. To solve this problem and to have one idea about the relationship between the different compounds we have used the concept of the formation energy, reported by Wolverton et al. [42],

$$\Delta E = E\left(\frac{1}{p+q} p H q\right) - p E f(M) - q E(H_2). \quad (1)$$

In equation (1), the amount  $\Delta E$  is the formation energy, the first term in the second member is the ground state energy of the crystal; the second is the metal ground state energy, and the last one is the energy of the molecular H. In Table 3 and Figures 1 and 2 are the values of the  $\Delta E$  as a function of the relation of the amount of H with respect to the total amount of atoms in the formula unit for the different Li-H and Be-H compounds, respectively,  $\Delta E$  is calculated in electron volts units. We have included the values coming from the FPLO calculations because



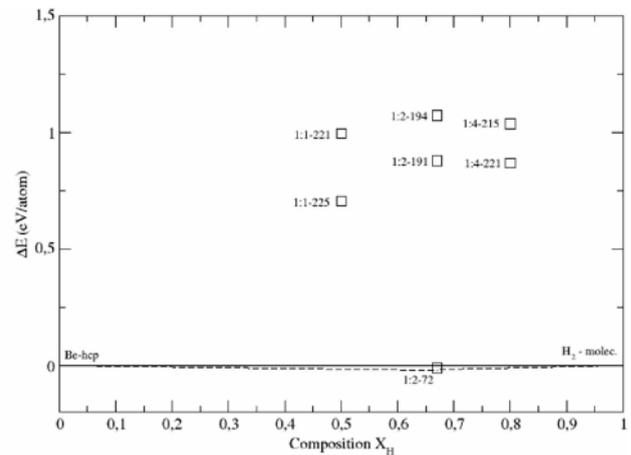
**Fig. 1.** The circles correspond to  $Li_{pHq}$  where  $p$  and  $q$  are the first and second number of the group, the third number is the number of the group of symmetry.

the differences between FPLO and LAPW values are to the second or third decimal, and the figures appear very confusing.

The contribution to the valence and conduction bands of the H and the metals are different, in the valence band we found, mainly, the 1s electrons of H, and a low contribution of Li and Be. The valence band consists a big part of the energy space of hybridization. In the conduction band are the electrons of the metals and in minor percentage the 1s of the H.

In Figures 1 and 2, we have drawn a line connecting the vertices of the convex hull [43–45], showing which are the stable compounds according the formation energies. The line begins at the stable crystal structure of Li-bcc and Be-hcp and ends in the stable phase in which the H, H<sub>2</sub>-molecular is found. The line touches the most negatives values of  $\Delta E$ , corresponding to the stable compounds, Li<sub>4</sub>H-221 and LiH-225, in the case of the Li-H series and BeH<sub>2</sub>-72 in the case of Be-H compounds. The other two compounds are below the zero value close to LiH-225, they are LiH-129 and LiH-221.

Hydrogen is an element whose Pauling electronegativity is 2.20 and is large compared with Be and Li which are 1.57 and 0.98, respectively. The stability of this compound can be explained by a function of the orbitals of the elements, Li has an electronic structure of  $1s^2 2s^1$ , the 1s orbital is very deep in the valence band, and 2s is between the valence and conduction band, the H is 1s', the only electron of H is mainly in the valence band, and is the electron that creates the bonds with other elements. The Be ( $1s^2 2s^2$ ) atomic orbitals have similar behavior to the atomic orbitals of Li in the analysis we developed. In Table 3 it is possible to see the population of the atomic orbitals of the different compounds. In the case of the three LiH (225, 129, 221) compounds which are the most stable, the 2s orbital of the Li, with only one electron, loses about 85% of the electronic charge, giving part of the charge to the 2p orbital (—20%) of the Li and about 60% to the 1s orbital of the H nearest neighbours. When this process does not occur and the amount of charge taken by the



the first and second number of the group, the third number is the number of the group of symmetry.

H is about 50% or less, the compounds are strongly unstable, in Figure 2 all these compounds are above of the value, then  $\Delta E = 0$ . The orbital 2p of Li, that originally was empty, when the compound is formed, receives part of the charge of the 1s orbital of the Li, and it participates in the stability of the compounds, in the case of LiH (1:1,  $p = 1$ ,  $q = 1$ ) the values of the population of this orbital are 0.252 for the 225, 0.211 for the 129 and 0.198 for the 221, respectively, these are in accordance with the position in Figure 2. The stabilities move away from the LiH-225 as the 2p of Li and 1s of H are less populated, jointly or alternatively. Similar behavior can be seen in the case of Be-H compounds, Table 3 and Figure 2. In the case of Li<sub>4</sub>H-221 ( $\Delta E = -0.048$ ) the transfer of the charge from Li-2s to Li-2p is very strong, the amount of charge captured by H-1s is not as great as in compounds 225, 221 and 129, in any way, with this combination the compound achieved a certain stability. A similar case is presented by the Li<sub>2</sub>H-221 ( $\Delta E = +0.019$ ), the difference here arises because the H-1s cannot capture enough charge of the Li-2s.

From another point of view, we can say that this phase diagram presents the meta-stability of the Li(Be)-H compounds, in particular of the LiH-221/129, with respect to the tie line from Li(Be) to H<sub>2</sub>. We can see from this figure the differences between both groups. In the group Li-H, LiH-221 is relatively close to the LiH-225, but LiH-129 with tetragonal structure is much closer to the 225, the difference in  $\Delta E$  is 0.15 eV, in the case of the LiH-221 the energetic difference is 0.25 eV with respect to the stable structure, but the theoretical transition pressure from LiH-225 to LiH-129 is much higher than the one to LiH-221. In the case of the Be-H compounds, all of them are very far from the synthesized compound BeH<sub>2</sub>-72, which indicates that all of them are unstable. On the other hand, it is well known that as a general rule those elements with an electronegativity ( $\chi$ ) varying between 1.35 and 1.82 do not form stable hydrides. In the present case, the electronegativities of the Li and the Be

**Fig. 2.** The squares correspond to  $Be_{pHq}$  where  $p$  and  $q$  are

are, 0.98 and 1.57, respectively, according to this rule the Li-H compounds have a greater chance of forming more stable compounds than those formed with Be-H. This assertion is not a good argument according to our calculation, because compounds with the same number of H atoms, in different phases, should have the same stability, but, according to the calculations shown in this work, that does not happen. The  $\Delta E$  value for BeH<sub>2</sub> has a very small negative value which gives an idea of the stability of this compound, in this case the calculation agrees with the non-stability criterion proposed using the hull line and the electronegativities.

#### 4 Conclusions

We have studied different compounds based on two materials Li-H or Be-H. For each of these groups we have proposed different amounts of H and different crystal structures, in that sense we are designing new compounds with the purpose of determining the formation energies and the different stabilities.

We have used two different methods of calculation with very different philosophies for the representation of the bases; the results of them are very close. The utilization of ab-initio codes and the very good results obtained on the compounds experimentally studied show that these kinds of tools give us a very powerful structure to predict new materials and their physical properties. The properties resulting from our results show a consistency which indicates the validity of the results and the methods used. Our first principles calculations do not negate the need for specific knowledge of these compounds, but give us trends of behaviors that serve to focus the possible solutions to the problem.

What we have tried to do, is find out the ranges of the stability of the different compounds belonging to each of the series studied. The total energies of the compounds can give us a lot of information about them; these amounts are not useful at the moment to evaluate the relative stabilities of the compounds. They are very important to describe the physical properties of known and unknown structures, in the latest case; we can predict the structural parameters, density of states, level of occupation of the orbitals, etc. But it is not the best parameter to describe the relative stabilities, in fact, lower total energy does not mean higher stabilities. The formation energies give us values to endorse the idea about the stabilities of the compounds. In this sense, we can see that in the case of the Li-H, the LiH-221 or LiH-129 are less stable than LiH-225. In the other series, BeH<sub>2</sub> is the one that remains stable. We have also seen that the charge transfer between orbitals is deeply linked to the stability of the compounds. For this, we must put in contact with the H, metals having a much lower electronegativity than H, favoring charge transfer. We can see that Be-H compounds are unstable whereas Li-H compounds are stable or quasi stable (225, 221). This can be seen as an indication that the Li-H compounds exhibit a better alternative than Be-H compounds for the use as H reservoirs.

de Ingeniería-Universidad Nacional de La Plata (FI UNLP), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and for the Grant I158 (UNLP).

#### References

1. E. Zurek, R. Hoffmann, N.W. Ashcroft, A.R. Oganov, A.O. Lyakhov, Proc. Natl. Acad. Sci. USA **106**, 17640 (2009)
2. F. Orecchini, Int. J. Hydrogen Energy **31**, 1951 (2006)
3. A. Züttel, Materials Today **6**, 24 (2003)
4. A. Züttel, Die Naturwissenschaften **91**, 157 (2004)
5. L. Schlapbach, A. Züttel, Nature **414**, 353 (2001)
6. L. Schlapbach, A. Züttel, P. Gröning, O. Gröning, P. Aebi, Appl. Phys. A **72**, 245 (2001)
7. P. Hohenberg, W. Kohn, Phys. Rev. B **136**, 864 (1964)
8. W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965)
9. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *An augmented plane wave + local orbitals program for calculating crystal properties* (Technical University of Vienna, Austria, 1999)
10. K. Koepnik, Phys. Rev. B **59**, 1743 (1999)
11. K. Koepnik, B. Velicky, R. Hayn, H. Eschrig, Phys. Rev. B **55**, 5717 (1997)
12. I. Opahle, K. Koepnik, H. Eschrig, Phys. Rev. B **60**, 14035 (1999)
13. J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)
14. A.D. Becke, E.R. Johnson., J. Chem. Phys. **124**, 221101 (2006)
15. F. Tran, P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)
16. D.P. Schumacher, Phys. Rev. **126**, 1679 (1962)
17. R. Dovesi, C. Ermondi, E. Ferrero, C. Pisani, C. Roetti, Phys. Rev. B **29**, 3591 (1984)
18. R. Napán, E.L. Peltzer y Blancá, Int. J. Hydrogen Energy **37**, 5784 (2012)
19. R. Ahuja, O. Eriksson, B. Johansson, Physica B **265**, 87 (1999)
20. U. Hantsch, B. Winkler, V. Milman, Chem. Phys. Lett. **378**, 343 (2003)
21. P. Ravindran, P. Vajeeston, H. Fjellvåg, A. Kjekshus, Comput. Mater. Sci. **30**, 349 (2004)
22. H.F. Zhang, Y. Yu, Y.N. Zhao, W.H. Xue, T. Gao, J. Phys. Chem. Solids **71**, 976 (2010)
23. D.K. Smith, H.R. Leider, J. Appl. Crystallography **1**, 246 (1968)
24. G.S. Smith, Q.C. Johnson, D.K. Smith, D.E. Cox, A. Zalkin, Solid State Commun. **67**, 491 (1988)
25. F.D. Murnaghan, Am. J. Math. **49**, 235 (1937)
26. J.L. Martins, Phys. Rev. B **41**, 7883 (1990)
27. J. Hama, K. Suito, N. Kawakami, Phys. Rev. B **39**, 3351 (1989)
28. Y. Wang, R. Ahuja, B. Johansson, Phys. Stat. Sol. B **235**, 470 (2003)
29. S. Baroni, G. Pastori Parravicini, G. Pezzica, Phys. Rev. B **32**, 4077 (1985)
30. Y. Kondo, K. Asaumi, J. Phys. Soc. Jpn **57**, 367 (1988)
31. S. Leb'egue, C.M. Araújo, O. Eriksson, B. Arnaud, M. Alouani, R. Ahuja, J. Phys.: Condens. Matter **19**, 036223 (2007)
32. P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvåg, J. Alloys Compd. **387**, 97 (2005)

33. B.-T. Wang, P. Zhang, H.-L. Shi, B. Sun, W.-D. Li, Eur. Phys. J. B **74**, 303 (2010)
34. S. Leb`egue, M. Alouani, B. Arnaud, W.E. Pickett, Europhys. Lett. **63**, 562 (2003)
35. A.B. Kunz, D.J. Mickish, Phys. Rev. B **11**, 1700 (1975)
36. D.J. Singh, Phys. Rev. B **82**, 205102 (2010)
37. M. Ahart, J.L. Yarger, K.M. Lantzky, S. Nakano, H.-K. Mao, R.J. Hemley, J. Chem. Phys. **124**, 14502 (2006)
38. F.E. Pretzel, G.N. Rupert, C.L. Mader, E.K. Storms, G.V. Gritton, C.C. Rushing, J. Phys. Chem. Sol. **16**, 10 (1960)
39. D.R. Stephens, E.M. Lilley, J. Appl. Phys. **39**, 177 (1968)
40. F. Perrot Bulk, Phys. Stat. Sol. B **77**, 517 (1976)
41. M. van Setten, G. de Wijs, G. Brocks. Phys. Rev. B **77**, 1 (2008)
42. C. Wolverton, V. Ozoliņš, M. Asta. Phys. Rev. B **69**, 1 (2004)
43. M. Widom, J.A. Moriarty, Phys. Rev. B **58**, 8967 (1998)
44. M. Mihalkovič, M. Widom, Phys. Rev. B **70**, 144107 (2004)
45. M. Widom, Phys. Rev. B **70**, 1 (2004)