

First principle calculations for improving desorption temperature in $\text{Mg}_{16}\text{H}_{32}$ doped with Ca, Sr and Ba elements

M BHIHI¹, M LAKHAL¹, S NAJI^{1,2}, H LABRIM³, A BELHAJ⁴, A BENYOUSSEF^{1,5,6}, A EL KENZ^{1,*}, M LOULIDI¹, B KHALIL¹, O MOUNKACHI⁵, M ABDELLAOUTI¹ and E K HLIL⁷

¹LMPHE (URAC 12), Faculté des Sciences, Université Mohammed V-Agdal, Rabat 10000, Morocco

²Department of Physics, Faculty of Science, Ibb University, Ibb 1120, Yemen

³Centre National de l'Energie, des Sciences et des Techniques Nucléaires, Rabat 10000, Morocco

⁴Département de Physique, Faculté Polydisciplinaire, Université Sultan Moulay Slimane, Béni Mellal 23000, Morocco

⁵Institute of Nanomaterials and Nanotechnology, MAScIR, Rabat 10000, Morocco

⁶Hassan II Academy of Science and Technology, Rabat 10000, Morocco

⁷Institut Néel, CNRS-UJF, 38042 Grenoble cedex 9, France

MS received 26 June 2013; revised 25 December 2013

Abstract. Using *ab initio* calculations, we predict the improvement of the desorption temperature and the hydrogen storage properties of doped Mg-based hydrides such as, $\text{Mg}_{15}\text{AMH}_{32}$ (AM = Ca, Sr and Ba) as a super cell $2 \times 2 \times 2$ of MgH_2 . In particular, the electronic structure has been obtained numerically using the all-electron full-potential local-orbital minimum-basis scheme FPLO9-00-34. Then, we discuss the formation energy calculations in terms of the material stabilities and the hydrogen storage thermodynamic properties improvements. Among others, we find that the stability and the temperature of desorption decrease without reducing significantly the high storage capacity of hydrogen. Moreover, it has been observed that such a doping procedure does not affect the electronic behavior as seen in MgH_2 , including the insulator state in contrast with the transition metal hydrides, which modify the electronic structure of pure MgH_2 .

Keywords. Electronic structure calculations; MgH_2 ; formation energy; hydrogen storage capacity; DFT; first principle calculations.

1. Introduction

The magnesium (Mg) based hydride is one of the most attractive materials for hydrogen storage applications due to its high gravimetric and volumetric capacities (7.65 wt% and 110 g H_2/l , respectively) for the stoichiometric binary MgH_2 (Shang *et al* 2003; Lakhali *et al* 2013). However, it has rather slow hydrogen absorption. The desorption kinetics as well as high dissociation temperature 573–673 K essentially reduces its application for hydrogen storage (Liang *et al* 1999). Various attempts have been made to improve the absorption and the desorption characteristics of magnesium hydride. Experimentally, it has been reported that mixing magnesium or magnesium hydride with small amounts of transition metals (TM) including their oxides radically accelerates the hydrogen kinetics (Mintz *et al* 1978). However, a slight decrease of the desorption temperatures has been observed (Song *et al* 2002; Rivoirard *et al* 2003; Charbonnier *et al* 2004; Shang *et al* 2004; Spassov *et al* 2005; Shao *et al* 2009; Xiao *et al* 2009).

In addition, the study of the electronic structure of Mg-based alloys hydrides is done to predict further

modifications destabilizing the corresponding hydrides by lowering the desorption temperature and enhancing the hydrogen kinetic characteristics. Several theoretical studies have been carried out to clarify the mechanisms with the help of alloying effects on the thermodynamic properties of the magnesium-based hydrides. The obtained results are in good agreement with the experimental literature (Moysès Araújo and Ahuja 2005; Hou 2006; Alapati *et al* 2007; Bouhadda *et al* 2007; Gremaud *et al* 2007; Velikokhatnyi and Kumta 2007; Xiao *et al* 2009; Bhihi *et al* 2012).

The aim of this work is to contribute to the improvement of hydrogen storage properties including absorption and desorption temperatures by studying the electronic structure of Mg-doped hydride with 2nd group ($\text{Mg}_{15}\text{AMH}_{32}$ where AM=Ca, Sr and Ba) using *ab initio* calculations based on the DFT techniques. As far as we know, it is the first time that such Mg-doped hydride material is considered to reduce the stability of the system. It is worth noting that the usual way has been devoted to exploring only the transition metals. Using an explicit calculation based on FPLO code, the formation energy and their hydrogen storage thermodynamic properties are explicitly computed. In particular, we discuss the hybridization between orbitals using density of state techniques. It follows that the doped system is less stable than

*Author for correspondence (elkenz@fsr.ac.ma)

the pure MgH_2 . Moreover, it has been shown that such a doping procedure allows the system to preserve the same electronic behavior as seen in MgH_2 , including the insulator state in contrast with the transition metal hydrides, which usually modify the electronic structure of pure MgH_2 .

2. Calculation method

In this paper, we use ab initio calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9-00-34 (www.fplo.de, Koepnik and Eschrig 1999). This has been done to solve the Kohn–Sham equations using the scalar-relativistic scheme. The parameterization of the exchange–correlation energy has been done within the generalized gradient approximations (Perdew and Wang 1992). To ensure a high accuracy in our computations, we have used both self-consistent criterions of the energy and density together with a precision of 10^{-8} Ha and 10^{-6} Ha $^{-1}$ Å $^{-3}$, respectively. To accurately perform Brillouin zone integrations, we have considered a $12 \times 12 \times 12$ K -point mesh. The valence basis state sets are (3s, 3p) and (1s) for Mg and H, respectively. Lattice parameters ‘ $a=b$ and c ’ have been optimized for each doped Mg-based hydride ($\text{Mg}_{15}\text{AMH}_{32}$) using the relaxation method, which will be discussed in the next section. Such parameters may be modified depending on the doped elements.

3. Results and discussion

3.1 Structural parameters and relaxation

We first relax the structural parameters using the relaxation method presented in our previous work (Bhihi et al 2012). In this calculation, we assume that the experimentally stable rutile structure of MgH_2 ($P42/mnm$, space group No. 136) is obtained with the Wyckoff position of Mg and H 2a (0, 0, 0) and 4f (0.304, 0.304, 0). First, we consider the lattice

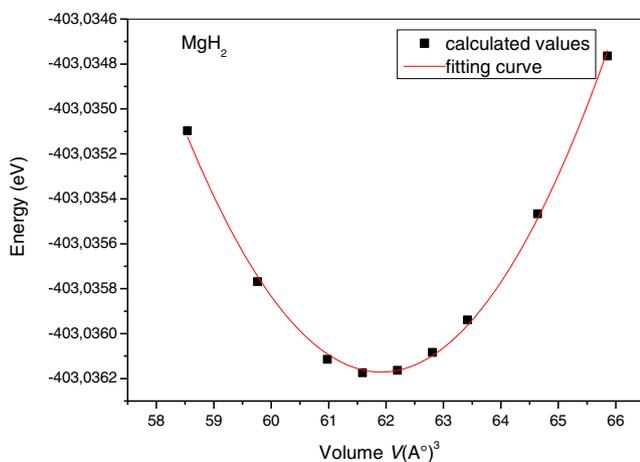


Figure 1. Total energy as a function of volume (V) of primitive cell.

parameters as $a = b = 4.501$ Å and $c = 3.01$ Å (Bortz et al 1999). Before performing the calculation, we start by relaxing our parameters; see figure 1. Indeed, we minimize the total energy to optimize such parameters. The calculated equilibrium values agree with results obtained by other groups (Bouhadda et al 2007; Bhihi et al 2012). Our results are given in table 1.

In order to reduce the overall doped atom concentrations, larger primitive supercells with $2 \times 2 \times 2$ stacked original MgH_2 unit cells have been used. In this atomic representation, one Mg atom, among the 16 existing in the supercell, is replaced by alkaline metal AM (AM = Ca, Sr and Ba) atoms. This corresponds to a 6.25% doping concentration. The concentration 12.5% has also been considered, see table 2.

This has been considered to investigate the influence of substitution on the total energy and the electronic structure. This new system will involve a special crystal symmetric structure ($Cmmm$ space group no. 65) with 17 non-equivalents site; see figure 2. This structure will allow us to compute the minimal total energy of the doped system to predict the heat of formation. The latter is needed to determine the stability of hydrides.

3.2 Hydrides stability: heat of formation

In this study, the heat of formation ΔH of Mg -based hydride, which is the most important thermodynamic parameter, has been calculated and used in order to predict new materials adopted to hydrogen storage. This can be obtained from the fact that it allows determining the heat of the hydrogenation reaction ($\Delta H < 0$ hydride is stable and vice versa), and deducing the temperature of desorption of the hydrogen in the studied system. We recall that the quantity ΔH of the hydride can be defined as the difference between the sum of total energy of products and the reactants (Xiao et al 2009):

$$\Delta H_{\text{HF}} = \sum E_{\text{tot}}(\text{products}) - \sum E_{\text{tot}}(\text{reactants}). \quad (1)$$

The reaction related to the formation of the hydride MgH_2 and $\text{Mg}_{15}\text{AMH}_{32}$ is as follows:

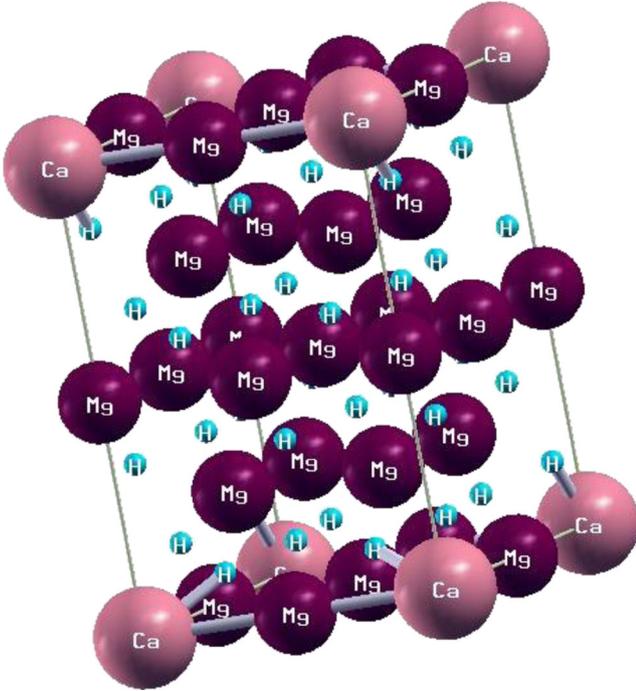


Table 1. Minimal total energy for optimized parameters of MgH_2 .

Minimal energy $E_{\text{min}}(\text{Ry})$	$a=b$ (Å)	c/a	Reference
-403.03609	4.524	0.66874	This work
-403.042937	4.519	0.66873	Bouhadda et al (2007)
-403.04777	4.585	0.6572	Bhihi et al (2012)
-	4.5176	0.6686	Maark et al (2012)
402.39 (i.e. 5474.854 eV)	4.5124	0.6701	Zhang et al (2010)
-	4.495	0.6685	Li et al (2006)
-	4.533	0.6686	Liang (2003)

Table 2. Total energy, heat of formation and desorption temperature of Mg₁₅AMH₃₂ (AM: alkaline metal).

System	Concentration (%)	Total energy (Ry)	Heat of formation kJ/mol (H ₂)	Desorption temperature (K)
Mg ₁₆ H ₃₂		-6448.577	-62.57	460.12
Mg ₁₅ CaH ₃₂	6.25	-7408.684	-60.82	447.19
Mg ₁₄ Ca ₂ H ₃₂	12.5	-8368.791	-59.05	434.24
Mg ₁₅ SrH ₃₂	6.25	-12407.445	-48.17	354.23
Mg ₁₄ Sr ₂ H ₃₂	12.5	-18366.3144	-33.85	248.90
Mg ₁₅ BaH ₃₂	6.25	-22326.185	-20.79	152.84
Mg ₁₄ Ba ₂ H ₃₂	12.5	-38203.8	-9.83	72.29

**Figure 2.** Crystal structure of Mg₁₅AMH₃₂ in primitive cell.

On the basis of these reactions, we have calculated the heat of formation of MgH₂ and Mg₁₅AMH₃₂ based on hydride according to the following formulas:

$$\Delta H = E_{\text{tot}}(\text{MgH}_2) - E_{\text{tot}}(\text{Mg}) - E_{\text{tot}}(\text{H}_2), \quad (4)$$

$$\Delta E_{\text{HF}} = E_{\text{tot}}(\text{Mg}_{15}\text{AMH}_{32}) - 15E_{\text{tot}}(\text{Mg}) + E_{\text{tot}}(\text{AM}) - 16E_{\text{tot}}(\text{H}_2). \quad (5)$$

The value of the total energy of the H₂ molecule $E_{\text{tot}}(\text{H}_2) = -2.320$ Ry has been taken from Shang *et al* (2004) and Nakamura *et al* (1998). The total energies per atom for pure elements have been calculated using the lattice parameters of Mg, Ca, Sr and Ba given in Kittel (1986).

Based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34 method, the calculated total energy and the heat of formation, in the magnesium hydride for optimized parameters structure, are

-6448.577 eV and -82.33 kJ/mol (H₂), respectively. These values are comparable with those obtained experimentally $\Delta H = -74.3 \pm 0.5$ kJ/mol H₂ (Friedlmeier and Bolcich 1988), -81.2 kJ/mol H₂ (Klose and Stuke 1995), -76.15 ± 9.2 kJ/mol H₂ (Vajeeston *et al* 2002) and $\Delta H = -68.00 \pm 9.2$ kJ/mol (Liang 2003). Such results, which are in good agreement with the experimental ones and with some theoretical values including $\Delta H = -55.648$ to -65.196 kJ/mol H₂ (i.e. -0.577 to -0.676 eV/H₂) (Zhang *et al* 2010) and $\Delta H = -71.1$ kJ/mol H₂, obtained recently in the literature (Liang 2003), validate our modeling approximations and the result obtained in our previous work (Bhihi *et al* 2012). The complete calculations of total energy, as well as the heat of formation of the studied new hydride, are listed in table 2. To reduce such values, in order to get unstable behavior, we have doped the system using the alkaline metals for 6.25% and 12.5% concentrations. For 6.25%, the total energy, and the heats of formation of the studied new hydride are -60.82, -48.17 and -20.79 kJ/mol H₂ for Mg₁₅CaH₃₂, Mg₁₅SrH₃₂ and Mg₁₅BaH₃₂, respectively. The same physical quantities have been given for 12.5%, see table 2. The obtained results show that when we increase the concentration of doping element the stability decreases. This is in agreement with the results reported by Bouaricha *et al* (2000) and Tanniru *et al* (2010) who found that for high concentrations (i.e. of greater than 10% of Al), these kinetics become increasingly important. Moreover, Shang *et al* (2003) have used concentration up to 10% of Nb to obtain good results. Also Shahi *et al* (2013) have used transition metals (TM: Ti, Fe and Ni) with different concentrations, they found that 5 wt% of TM gave the best results.

It follows from these calculations that the concentration also plays a crucial role in decreasing the stability (see table 2). The implementation of the alkaline earth metals to MgH₂ reduces the stability of MgH₂, leading to an improvement of the dehydrogenation kinetics.

3.3 Desorption temperature

The thermodynamic properties of the hydrides are described by the standard Gibbs energy:

$$\Delta G = \Delta H - T \Delta S, \quad (6)$$

where ΔH and ΔS ($\Delta S \approx \Delta S(\text{H}_2) = 130.7 \text{ J/mol K}$) are the heat formation and the entropy change of the dehydrogenation reaction, respectively. At the decomposition temperature for a constant pressure, the standard Gibbs energy becomes zero. Therefore, the temperature of the dehydrogenation can be estimated according to $\Delta H = T \Delta S$ (Bhihi et al 2012).

The calculations presented in this study show that for pure MgH_2 the decomposition temperature is equal to 460.12 K, which is close to other values 573–673 K found in Shang et al (2003, 2004) and Bhihi et al (2012). On the other hand, alloying MgH_2 with small amounts of alkaline metals can have a great effect in destabilizing the parent compound MgH_2 by lowering the decomposition temperature, without significantly reducing its high hydrogen capacity (see table 3).

It has been observed that the temperature of desorption decreases according to the augmentation Z number of the elements appearing in the second group and in decreasing order of the electronegativity. It follows from figures 3–6 and tables 4 and 5 that the band gap decreases from Mg to Ba. This could be explained by the decreasing of the electronegativity.

3.4 Electronic structure

The density of state has been used to understand and explain the nature of metals in the alloys hydride $\text{Mg}_{15}\text{AMH}_{32}$. In

Table 3. Gravimetric hydrogen capacities of $\text{Mg}_{15}\text{AMH}_{32}$ (AM = alkaline metal).

System	Gravimetric hydrogen capacities (wt%)
$\text{Mg}_{16}\text{H}_{32}$	7.65
$\text{Mg}_{15}\text{CaH}_{32}$	7.38
$\text{Mg}_{15}\text{SrH}_{32}$	6.66
$\text{Mg}_{15}\text{BaH}_{32}$	6.04

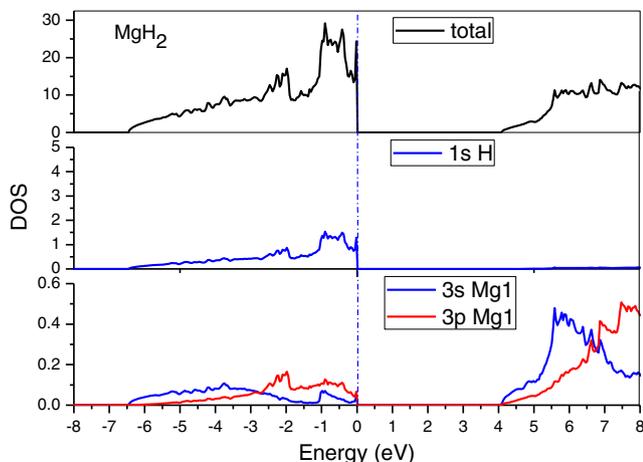


Figure 3. Total and partial DOSs of MgH_2 .

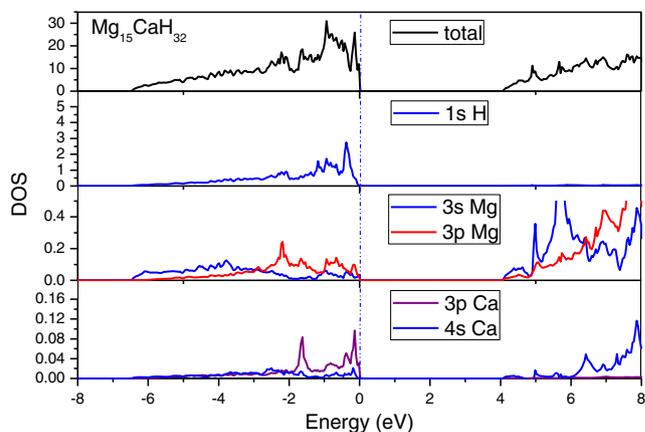


Figure 4. Total and partial DOSs of $\text{Mg}_{15}\text{CaH}_{32}$.

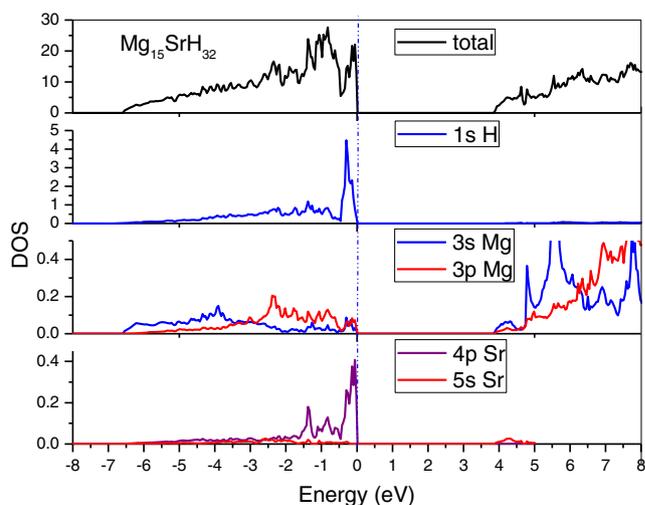


Figure 5. Total and partial DOSs of $\text{Mg}_{15}\text{SrH}_{32}$.

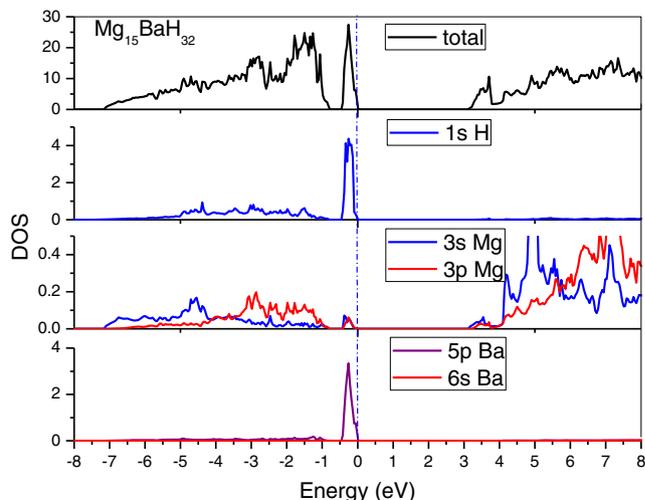


Figure 6. Total and partial DOSs of $\text{Mg}_{15}\text{BaH}_{32}$.

Table 4. Electronegativity per atom for alkaline metal.

Elements	Electronegativity in Pauling unit
Mg	1.31
Ca	1.00
Sr	0.95
Ba	0.89

Table 5. Energy gap and width of valance band for each system, $Mg_{15}AMH_{32}$ (AM= alkaline metal).

System	Width of valance band (VB) (eV)	Gap energy (eV)
MgH_2	6.426	4.059
$Mg_{15}CaH_{32}$	6.466	4.052
$Mg_{15}SrH_{32}$	6.586	3.850
$Mg_{15}BaH_{32}$	7.147	3.116

particular, it has been explored to clarify their effect on the stability and the kinetics of hydrogen absorption–desorption.

For this reason, the total (DOS) and the partial density of electronic states (P-DOS) of MgH_2 , with and without additional metals (AM=Ca, Sr and Ba), have been calculated. Our calculation is plotted in figures 3–6. On the one hand, it follows from figure 3 that there are two parts in the valance band (VB). In the first part, the band with energy range from -1.8 to 0.0 eV is called ‘high VB’ composed mainly of strongly hybridized H-1s and Mg-3p states. The second part concerns the band with energy range from -6.42 to -1.8 eV which is called ‘lower VB’ originating almost from Mg-3s and H-1s states. While the contribution of the lowest conduction band (CB) is fully from Mg-3p, Mg-3s and few H-1s states. On the other hand, we can observe that the obtained energy gap (E_g) is 4.06 eV, which is typical for an insulating system. Up to a difference of the order of 1 eV, our value and those obtained by the GGA approximation 3.9 eV (Kelkar *et al* 2008; Zhang *et al* 2010), 4.0 eV (Li *et al* 2006) and 4.2 eV (Vajeeston *et al* 2002) are close to the experimental one 5.16 eV given in Yu and Lam (1988). Indeed, this value has been improved by using the GW approximation 5.58 eV (Zhang *et al* 2010).

For MgH_2 doped with alkaline metal, we start by studying the effect of the nature of the alkaline metals (AM) on the electronic structure of MgH_2 . To make a comparison between the nature of this metal and MgH_2 , we plotted, in figures 4–6, the total and partial DOSs of MgH_2 -doped alkaline metals (AM=Ca, Sr and Ba). From these figures, we observe that the overall shapes of the total DOSs for $Mg_{15}AMH_{32}$ (AM=Ca, Sr and Ba) are similar to each other. When doping with alkaline metals, the system preserves the same electronic behavior as seen in pure MgH_2 (Maark *et al* 2012). In particular, the doped system keeps the

insulator state. In contrast, the transition metal hydrides modify the electronic structure of MgH_2 which is converted to a metallic structure as reported in Xiao *et al* (2009) and Li *et al* (2006).

The only small difference between different components is seen in the hybridization between H-1s and p state of metal elements. It becomes more and more localized near the Fermi level according to the following order:

$$Mg \rightarrow Ca \rightarrow Sr \rightarrow Ba. \quad (7)$$

Moreover, the valance band is mainly attributed to H-1s states and the introduction of the doped element has increased the width of the VB according to the above order (7). Comparing the density of states of the second group alkaline metal hydrides including $Mg_{15}CaH_{32}$, $Mg_{15}SrH_{32}$ and $Mg_{15}BaH_{32}$, we find that the $Mg_{15}CaH_{32}$ has the smallest DOS localisation near Fermi level due to the hybridization between Ca-3p and H-1s. While for $Mg_{15}SrH_{32}$, the hybridization between Sr-4p and H-1s is more localized than the Ca one. Then, this localization of H orbital becomes very important for $Mg_{15}BaH_{32}$, resulting from hybridization between Ba-5p and H-1s. This indicates that the localization of H-1s states comes from strong local hybridization between AM-p and H-s states. Also the hybridization between Mg-s and H-s states, which constitutes the lower VB becomes slightly weaker. This leads to a decreasing of the stability of the hydride. This is consistent with heat of the formation energy calculations listed in table 2. Moreover, we can see that the obtained energy gap (E_g) decreases following the same order as in (7). For each element, the energy gap calculation is summarized in table 5.

4. Conclusions

In this paper, we have discussed the H desorption mechanism within the hydrides using the electronic structure calculations based on the ab-initio method. Among others, we have found that the localization of H-s states near Fermi level, obtained from the hybridization between AM and H atoms, is mainly responsible for the gap width tuning and the destabilization of the system. Moreover, the comprehension of hydrogen desorption allowed us to estimate the formation energy and the temperature values of the H desorption. The calculated quantities agree with the experimental data given in Shang *et al* (2003, 2004). Such estimated values allow us to consider that the component $Mg_{15}SrH_{32}$ is the most appropriate material for H desorption near room temperature without losing much in terms of storage capacity. Moreover, we have observed that the stability system decreases in accordance with the decreasing of the electronegativity of the doped elements. In particular, it has been realized that such doping procedures with alkaline metals, in contrast to the transition metals (Li *et al* 2006; Xiao *et al* 2009), do not change the electronic structure as seen in MgH_2 including the insulator state.

Acknowledgements

This work was supported by CNRST in the framework of the National Program Dev-RS/04. The authors acknowledge its financial support.

References

- Alapati S V, Johnson J K and Sholl D S 2007 *J. Alloys Compd.* **446–447** 23
- Bhihi M, Lakhali M, Labrim H, Benyoussef A, El Kenz A, Mounkachi O and Hlil E K 2012 *Chin. Phys. B* **21** 097501
- Bortz M, Bertheville B, Bottger G and Yvon K 1999 *J. Alloys Compd.* **287** L4
- Bouaricha S, Dodelet J P, Guay D, Huot J, Boily S and Schulz R 2000 *J. Alloys Compd.* **297** 282
- Bouhadda Y, Rabehi A and Bezzari-Tahar-Chaouche S 2007 *Revue des Energies Renouvelables* **10** 545
- Charbonnier J, de Rango P, Fruchart D, Miraglia S, Pontonnier L, Rivoirard S, Skryabina N and Vulliet P 2004 *J. Alloys Compd.* **383** 205
- Friedlmeier G M and Bolcich J C 1988 *Int. J. Hydrogen Energy* **13** 467
- Gremaud R, Broedersz C P, Borsa D M, Schreuders H, Rector J H, Dam B and Griessen R 2007 *Adv. Mater.* **19** 2813
- Hou Z F 2006 *J. Power Sources* **159** 111
- Kelkar T, Pal S and Kanhere D G 2008 *Chem. Phys. Chem.* **9** 928
- Kittel C 1986 *Introduction to solid state physics* (New York: Wiley)
- Klose W and Stuke V 1995 *Int. J. Hydrogen Energy* **20** 309
- Koepernik K and Eschrig H 1999 *Phys. Rev. B* **59** 1743
- Lakhali M, Bhihi M, Labrim H, Benyoussef A, Naji S, Belhaj A, Khalil B and Abdellaoui M 2013 *Int. J. Hydrogen Energy* **38** 8350
- Li S, Jena P and Ahuja R 2006 *Phys. Rev. B* **74** 132106
- Liang J-J 2003 *Fuel Chemistry Division Preprints* **48** 28
- Liang G, Huot J, Boily S, Van Neste A and Schulz R 1999 *J. Alloys Compd.* **292** 247
- Maark T A, Hussain T and Ahuja R 2012 *Int. J. Hydrogen Energy* **37** 9112
- Mintz M H, Malkiely S, Gavra Z and Hadari Z 1978 *J. Inorg. Nucl. Chem.* **40** 1949
- Moysès Araújo C and Ahuja R 2005 *J. Alloys Compd.* **220** 404
- Nakamura H, Nguyen-Manh D and Pettifor D G 1998 *J. Alloys Compd.* **281** 81
- Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- Rivoirard S, de Rango P, Fruchart D, Charbonnier J and Vempaire D 2003 *J. Alloys Compd.* **622** 356
- Shahi R R, Tiwari A P, Shaz M A and Srivastava O N 2013 *Int. J. Hydrogen Energy* **38** 2778
- Shang X, Bououdina M and Guo Z X 2003 *J. Alloys Compd.* **349** 217
- Shang X, Bououdina M, Song Y and Guo Z X 2004 *Int. J. Hydrogen Energy* **29** 73
- Shao H, Asano K, Enoki H and Akiba E 2009 *J. Alloys Compd.* **477** 301
- Song M Y, Bobet J L and Darriet B 2002 *J. Alloys Compd.* **340** 256
- Spasov T, Rangelova V, Solsona P, Baró M D, Zander D and Köster U 2005 *J. Alloys Compd.* **398** 139
- Tanniru M, Slattery D K and Ebrahimi F 2010 *Int. J. Hydrogen Energy* **35** 3555
- Vajeeston P, Ravindran P, Kjekshus A and Fjellvåg H 2002 *Phys. Rev. Lett.* **89** 175506
- Velikokhatnyi O I and Kumta P N 2007 *Mater. Sci. Eng. B* **140** 114
- Xiao X-B, Zhang W B, Yu W Y, Wang N and Tang B Y 2009 *Physica B* **404** 2234
- Yu R and Lam P K 1988 *Phys. Rev. B* **37** 8730
- Zhang J, Huang Y N, Long C G, Zhou D N and Liu J S 2010 *Mater. Sci.-Poland* **28** 357