

# The Influence of Boron Doping Concentration on MgH<sub>2</sub> Electronic Structure

S. KURKO<sup>a,\*</sup>, B. PASKAŠ-MAMULA<sup>b</sup>, LJ. MATOVIĆ<sup>a</sup>, J. GRBOVIĆ NOVAKOVIĆ<sup>a</sup>, N. NOVAKOVIĆ<sup>b</sup>

<sup>a</sup>University of Belgrade, Vinča Institute of Nuclear Sciences, Laboratory for Material Sciences

P.O. Box 522, 11001 Belgrade, Serbia

<sup>b</sup>University of Belgrade, Vinča Institute of Nuclear Sciences, Laboratory for Nuclear and Plasma Physics

P.O. Box 522, 11001 Belgrade, Serbia

We have performed *ab initio* electronic structure calculations of Mg<sub>1-x</sub>B<sub>x</sub>H<sub>2</sub> compounds with different boron concentrations, ranging from  $x = 0.0625$  to  $0.5$ . Full structural relaxation was performed in order to properly describe influence of dopant on host matrix. Results showed that there is a strong influence of boron concentration on structural and thermodynamic stability of compound. B-H bond length is substantially shorter than in Mg-H coordination polyhedron. Boron significantly contributes to density of states at Fermi level within energy gap. The width of boron electronic states heavily depends on boron concentration, causing reduction of energy gap of host MgH<sub>2</sub>, and leading to metallic nature of compound with highest boron concentration. The predicted thermodynamic instability of compounds with higher boron concentration is in agreement with experimental findings that under similar stoichiometry, boron with magnesium forms only complex hydride, Mg(BH<sub>4</sub>)<sub>2</sub>. It is also shown that existence of stable hydrides with MgH<sub>2</sub> rutile structure and small concentration of boron is possible in principle and that boron can be used to further destabilize MgH<sub>2</sub> in order to enhance its hydrogen sorption-desorption kinetics.

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## 1. Introduction

Severe theoretical and experimental attempt has focused on the possibility to find a new hydrogen-storage material with high storage capacity and efficiently reversible storage. One of the approaches is hydrogen storage in various borohydrides of first and second group. However alkali borohydrides have relatively high temperature of desorption [1]. As typical representative of earth-alkaline borohydrides, Mg(BH<sub>4</sub>)<sub>2</sub> emerges as a promising candidate for hydrogen storage because of its high gravimetric storage density (14.8 wt%) and lower hydrogen binding enthalpy [2, 3]. It was found that the enthalpy and entropy of hydrogen desorption reaction should give 1 bar of equilibrium pressure for hydrogen at room temperature [4–7]. The low enthalpy of decomposition suggests a possibility of reversible hydrogen storage in this compound [6–8]. Nevertheless, there is high kinetic barriers involved in the hydrogen desorption, leading to a high operation temperature ( $> 270$  °C) and poor kinetics. Also, hydrogen desorption reaction is found to be rather complex, consisting of few steps [5] and full reversibility of rehydrogenation reaction is not achieved yet. In addition, full understanding of hydrogen sorption-desorption

process is limited owing to complicated crystal structure and difficulties to find exact positions of hydrogen in this compound. An effort has been made to resolve this using combined approach involving X ray and neutron diffraction measurements [9].

On the other hand, MgH<sub>2</sub> is well known to have high hydrogen gravimetric storage density. This material has rather simple structure as well. The problem is its high thermodynamic stability (formation enthalpy  $\sim 75$  kJ/molH<sub>2</sub> [10]), so the most of research efforts was put toward the ways of efficient and cost effective destabilization of MgH<sub>2</sub> matrix through various dopants introduction, mechanical or even ion beam modification [11–15].

The goal of our work was to investigate the interaction of boron with MgH<sub>2</sub> host matrix, where boron acts as dopant at various concentrations, substituting Mg in its octahedral hydrogen environment.

## 2. Details of electronic structure calculations

For calculations presented in this paper an Abinit [16, 17] pseudopotential code was used. Supplied LDA (Troullier-Martins) pseudopotentials were used for all constituent atoms. First, a full relaxation of rutile MgH<sub>2</sub> was performed. Then, thus obtained cell parameters and fraction coordinates were used for construction

\* corresponding author; e-mail: skumric@vinca.rs

of supercells of dopant systems. Force minimization due to ion positions was performed in all cases, but without volume optimization in case of supercell calculations. In case of MgBH<sub>4</sub> (50 at. % B), no supercell approach was needed, so full relaxation including volume optimization was also performed. Energy cut-off parameter  $E_{\text{cut}}$  and k point grid was chosen as a result of appropriate convergence studies.  $E_{\text{cut}}$  is chosen to be 20 Hartree for pure MgH<sub>2</sub>, and 30 Hartree in all other cases. K point sampling was done with  $8 \times 8 \times 8$  grid for MgH<sub>2</sub>,  $6 \times 6 \times 6$  for MgBH<sub>4</sub>,  $8 \times 8 \times 2$  in case of Mg<sub>4</sub>BH<sub>10</sub>, and  $6 \times 6 \times 8$  in case of Mg<sub>15</sub>BH<sub>32</sub>. Force minimization tolerance was  $5.0 \times 10^{-5}$  Hartree/Bohr, while energy tolerance within every SCF cycle was chosen to be  $10^{-6}$  Hartree. Structural optimization was performed using Broyden–Fletcher–Goldfarb–Shanno minimization (BFGS).

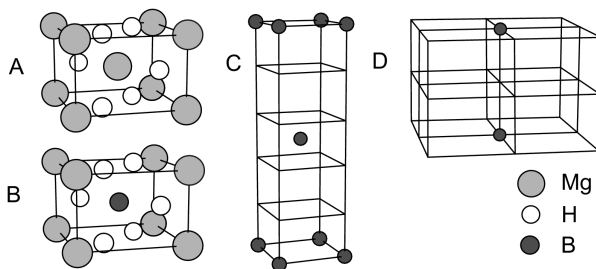


Fig. 1. Unit cells of investigated compounds a) pure MgH<sub>2</sub>, b) MgBH<sub>4</sub>, c) Mg<sub>4</sub>BH<sub>10</sub> and d) Mg<sub>15</sub>BH<sub>32</sub>. For c) and d) only unit cells stacking is shown, with positions of boron atoms.

In order to embed boron at various concentrations into MgH<sub>2</sub> host matrix, supercell approach was imposed. Four structures were subjects of investigation:

- pure MgH<sub>2</sub> rutile crystal structure
- MgBH<sub>4</sub> (50 at% B)
- Mg<sub>4</sub>BH<sub>10</sub> (20 at% B)
- Mg<sub>15</sub>BH<sub>32</sub> (6.25 at% B).

Pure MgH<sub>2</sub> compound has crystal structure of rutile (space group number 136, P4<sub>2</sub>/mnm, see Fig. 1a). MgBH<sub>4</sub> was obtained by substitution of one of two Mg atoms in original unit cell, thus lowering the symmetry (space group number 65, Cmmm, see Fig. 1b).

For construction of lower boron concentration structures, supercell approach was used. For Mg<sub>4</sub>BH<sub>10</sub> compound, supercell of five original unit cells was constructed, in structural arrangement  $5 \times 1 \times 1$  (space group number 136, P4<sub>2</sub>/mnm). The boron atoms are positioned at corners and at center of supercell (Fig. 1c).

Finally, for Mg<sub>15</sub>BH<sub>32</sub> compound, supercell of eight unit cells was constructed, in structural arrangement  $2 \times 2 \times 2$  (space group number 65, Cmmm). The dopant

atoms are positioned at center of two of supercell base planes (see Fig. 1d).

Enthalpies of formation for different fractional concentrations of B were calculated according to formula:

$$\Delta H_f(\text{Mg}_{1-x}\text{B}_x\text{H}_2) = E_{\text{tot}}(\text{Mg}_{1-x}\text{B}_x\text{H}_2) - (1-x)E_{\text{tot}}(\text{Mg}) - xE_{\text{tot}}(\text{B}) - E_{\text{tot}}(\text{H}_2). \quad (1)$$

### 3. Results and discussion

Densities of states (DOS) are shown in Fig. 2. for all four investigated systems. Moderate initial total number of available states in code is the reason for rather incomplete description of conduction bands. However, this is not relevant for present discussion. DOS of pure MgH<sub>2</sub> shows typical insulating behavior with wide energy gap, in this particular case estimated to be 3.6 eV. Underestimation of energy gap compared to experimental find-

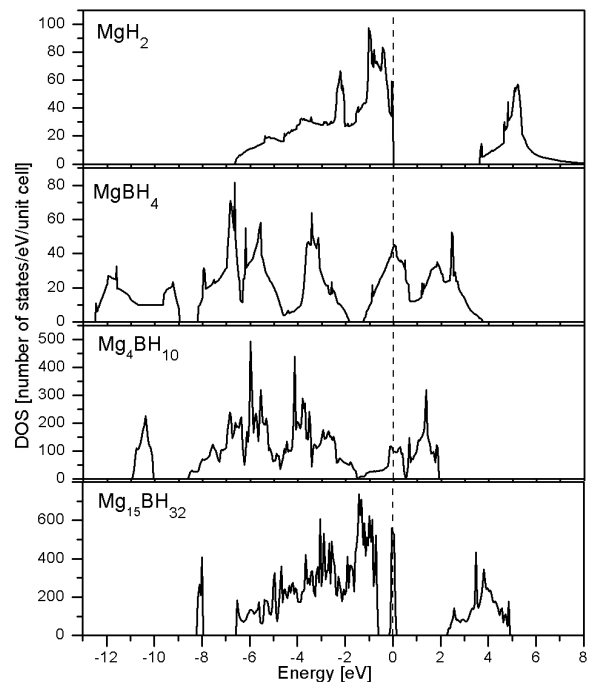


Fig. 2. Total densities of states for all four investigated systems. Fermi level is marked with vertical dashed line.

ings ( $\sim 5$  eV and more [18]) is expected for this kind of calculation (DFT LDA). Densities of states of other systems reveal certain trends. First, the narrowing of low energy feature with predominantly B contribution (at approx.  $-8$  eV for Mg<sub>15</sub>BH<sub>32</sub>) is evident, with decreasing of B concentration. Further, only at sufficiently low concentration of B (again for Mg<sub>15</sub>BH<sub>32</sub>), DOS resembles the one of pure MgH<sub>2</sub> system. The overall structure of pure compound is preserved, with two clearly visible superposed B originated localized states. Introduction of boron has moved Fermi level higher from top of valence band, so this level now coincides with higher narrow B states within energy gap. The observed trend in B states

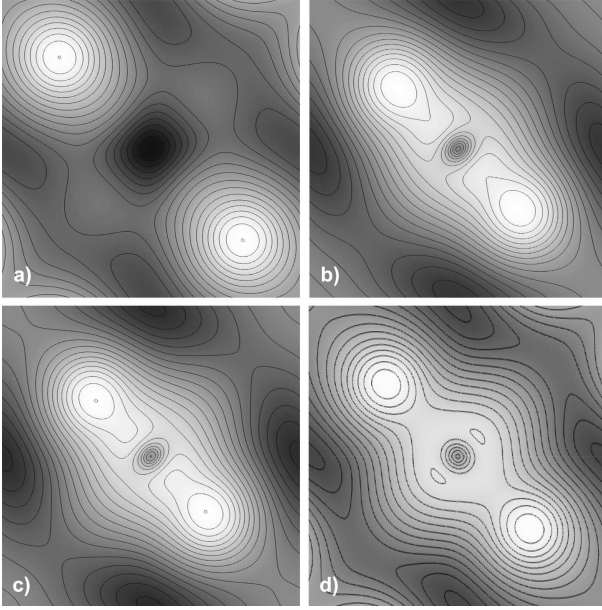


Fig. 3. Charge densities in the plane parallel to [001], containing the central atom site. a)  $\text{MgH}_2$ , b)  $\text{MgBH}_4$ , c)  $\text{Mg}_4\text{BH}_{10}$  and d)  $\text{Mg}_{15}\text{BH}_{32}$ . In case of a) the central atom is Mg, in three other cases it is B. On the square diagonal are two nearest neighbor H atoms.

widening with B concentration increase has the effect of essential filling of energy gap, leading to metallic nature of higher concentrated dopant systems. In Table, calculated enthalpies of formation are given, along with some structural parameters and derived parameters. The nearest neighbor octahedron of Mg in pure  $\text{MgH}_2$  consists of  $2 + 4$  nonequivalent H sites at almost identical distances from central Mg atom. After structure relaxation, corresponding B-H distances are considerably smaller compared to ones of pure compound, which can be attributed

to small ionic radius of boron and consequent contraction of B-H distances. Further, B-H nearest neighbor distances corresponding to nonequivalent H atoms are no longer equal, the difference becoming more pronounced with rise of dopant concentration.

The trend of sudden rise of enthalpy of formation value with increase of B concentration is evident. Only the structure with lowest concentration of B is thermodynamically stable, having still considerable negative enthalpy of formation. This can be attributed to the fact that in this structural arrangement, boron atom is forced to be in octahedral environment, thus having 6 nearest neighbor H atoms. At lowest B concentration this has minor impact on structure stability, which is not the case for other systems with higher B concentration. On Fig. 3 valence charge density maps for all four calculated compounds are shown, corresponding to the crystallographic plane parallel to [001] plane and shifted by  $1/2 c$  along  $z$  direction. On Fig. 3a, corresponding to pure  $\text{MgH}_2$ , plane contains central Mg and surrounding two H atoms.

This is a picture of typical ionic bonding, with depleted regions (dark) corresponding to Mg as electron donor, and electron rich regions corresponding to H atoms, without shared charge regions. Significant covalent contribution exists though, between H atoms at distance short enough to allow non negligible overlapping of states. The picture is different on Figs 3 b,c,d, containing the same plane, but with B as a central atom. H atoms are shifted closer to B atom, with significant amount of shared charge, donated by B atom. H atoms are essentially brought closer and are stronger bonded then in case of central Mg atom. This in turn causes weaker H-H bonding and destabilization of overall  $\text{MgH}_2$  matrix. Decrease of this shared charge density is visible on Figure 3 c and d, and is connected with fall of B concentration. This effect can explain trend in enthalpy of formation as a function of boron doping concentration.

TABLE

Some structural parameters and calculated enthalpies of formation of all investigated systems. Present calculation results are shown as **bold**.

Structure	Cell parameters		Distances [Å]		Space group		$\Delta H_f$ [kJ/molH <sub>2</sub> ]
	$a$ [Å]	$c$ [Å]	M-H1	M-H2	Number	Symbol	
$\text{MgH}_2$	<b>4.465</b>	<b>2.986</b>	<b>1.919*</b>	<b>1.919*</b>	136	P4 <sub>2</sub> /mnm	<b>-80.90</b>
	4.518 <sup>a</sup>	3.022 <sup>a</sup>					-76.15 <sup>a</sup>
	4.515 <sup>b</sup>	3.019 <sup>b</sup>	1.952 <sup>b</sup>	1.953 <sup>b</sup>			-69.51 <sup>b</sup>
$\text{Mg}_{15}\text{BH}_{32}$	8.930	5.972	1.476	1.544	65	Cmmm	-52.47
$\text{Mg}_4\text{BH}_{10}$	4.465	14.930	1.427	1.508	136	P4 <sub>2</sub> /mnm	+3.83
$\text{MgBH}_4$	4.138	2.767	1.279	1.637	65	Cmmm	+128.67

<sup>a</sup> experimental value [18], <sup>b</sup> calculated values (APW+lo method) [12], M = B except \* where M = Mg

#### 4. Conclusion

We have performed electronic structure calculations of three  $\text{MgH}_2$ :B dopant systems with various concentration of boron. For comparison, electronic structure calcula-

tion of pure  $\text{MgH}_2$  system has been done as well. Results showed that introduction of B destabilizes initial structure, and trend of sudden rise of enthalpy of formation with increase of B concentration is observed. However at

sufficiently low B concentration, the calculation predicts existence of stable dopant system. Its still considerably high stability can be further decreased by slight increase of B concentration.

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