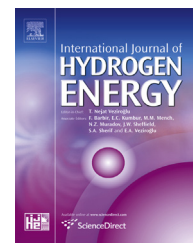




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# Theoretical study on the effects of the magnesium hydride doping with cobalt and nickel on the hydrogen release

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## ABSTRACT

We present the results of our DFT-based investigations on the effects of the substitution of magnesium with cobalt and nickel in the magnesium hydride on the bulk properties and on the hydrogen adsorption and desorption on the MgH<sub>2</sub>(001) surface. We present the energetic aspects of these interactions. Our calculations point to the merit of the cobalt and nickel dopants in the magnesium hydride destabilization, which facilitates the hydrogen release.

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## Introduction

The design of new materials with a high hydrogen content and the development of new and efficient methods for the controlling and the optimization of the hydrogen release by the manipulation of thermodynamic and kinetic conditions of the materials are essential in establishing the optimum and safe technological solutions for the production, storage, transportation and usage of hydrogen [1]. The traditional couple theory - experiment enables us to understand the interaction mechanisms and the phenomena that take place in bulk, on the surface, at the interface of different materials or at the

grain boundaries, as well as to establish the analytical equations and to characterize material properties. The atomistic and quantum simulations are essential in the thermodynamic and kinetic analysis of the bulk, surface and interface phenomena of the energy materials [2]. Computer simulations have been successfully applied to the study of the hydrogen adsorption [3] and dissociation [4] on the Mg(0001) surface, to the penetration of hydrogen into magnesium and the formation of the magnesium hydrate [5], to the electronic and structural properties of magnesium hydride [6] and their modification by doping and alloying [7–10]. A large number of theoretical studies are dedicated to the electronic and the structural properties of the magnesium hydride surfaces, to

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the hydrogen diffusion on surface [11] or through the interface Mg–MgH<sub>2</sub> [12] and to the hydrogen desorption [13] and its enhancement by the doping of the surface [14,15].

In the present study we report the results obtained by a DFT investigation, which aims at understanding the modification of the energy-derived properties of the magnesium hydride by doping it with cobalt and nickel atoms, with the aim to control the release of the hydrogen contained in the magnesium hydride. Also, we analyse different aspects of the surface doping and its influence on the hydrogen adsorption and desorption.

## Computational methods

### System models

At room temperature the magnesium hydride is an ionic compound and has the rutile structure, called  $\beta$ -MgH<sub>2</sub>. At high pressure it forms other two structures:  $\alpha$ -MgH<sub>2</sub> and  $\gamma$ -MgH<sub>2</sub> [16]. In the present study we only consider the structure  $\beta$ -MgH<sub>2</sub>, whose symmetry is described by the group P42/mnm (symmetry group no. 136), with the cell parameters  $a = 4.501$  Å and  $c = 3.010$  Å [16,17]. The primitive cell contains two magnesium atoms that occupy the 2a sites (0,0,0) and (1/2,1/2,1/2) and four hydrogen atoms at sites 4f ( $\pm x, \pm x, 0$ ) and ( $1/2 \pm x, 1/2 \pm x, 1/2$ ), with  $x = 0.304$  (see Fig. 1a).

The establishment of the most stable doped structure is beyond our aim, as we are only interested to analyse the effects of the substitution of magnesium with cobalt or nickel atoms at low concentration about 10%. This concentration corresponds to the replacement of one magnesium atom of eight.

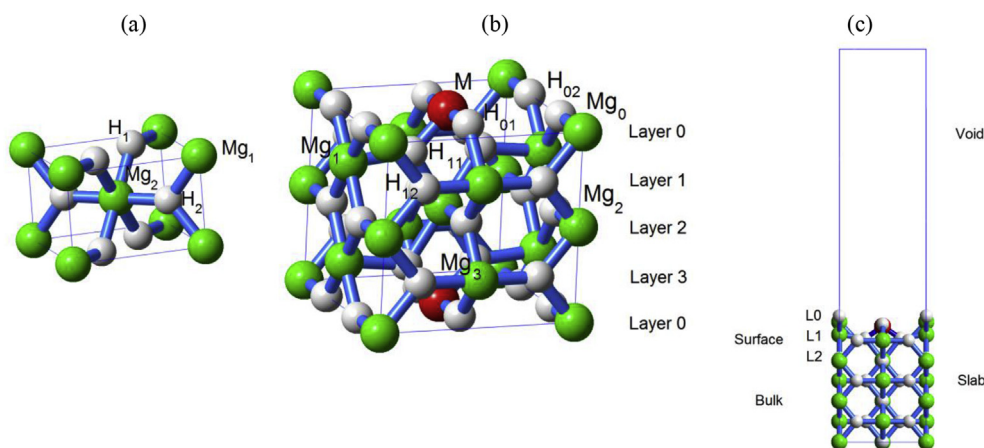
In the present study we use for the bulk calculations an almost cubic supercell ( $\sqrt{2} \times \sqrt{2}$ )R45° × 2 that contains 8 magnesium atoms and 16 hydrogen atoms. We use the notation M–Mg7H16 to indicate the investigated systems for the

clean (M = Mg) and the doped magnesium hydride (M = Co and Ni). Notations of various sites, based on the relative position to the atom M, are indicated in the Fig. 1b. We considered only the neutral hydrogen vacancies, although the vacancy may remain electrically charged [18].

In order to model the adsorption and desorption of the hydrogen atoms on the surface (001) we use the slab method, by creating a slab starting from the bulk optimized supercell ( $\sqrt{2} \times \sqrt{2}$ )R45° × 2, adding another half of cell along the  $c$ -axis. Thus, the slab has seven layers and consists in one atom M = Mg, Co or Ni, 13 magnesium and 28 hydrogen atoms. The number of layers in the slab is large enough to ensure the convergence of the surface energy [15]. The odd and even layers are equivalent, thus it is not important how we cut the surface. The atoms in the two top layers L0 and L1 (see Fig. 1c) are completely relaxed and the atoms in the third layer L2 are relaxed only along the  $c$ -axis, perpendicular to the surface. The other atoms are fixed in their bulk optimized position. A void domain of 20 Å is included to separate the image slabs along the  $c$ -axis. The size (lattice constants  $a = b = 6.4085$  Å and  $c = 29.0843$  Å) and the shape (angles  $\alpha = \beta = \gamma = 90^\circ$ ) are fixed during the optimization procedures of the surface system.

### Computing scheme

All the calculations were done with the Density Functional Theory code VASP [19], using the generalized gradient approximation with the PW91 exchange-correlation functional [20]. In order to reduce the calculation efforts, the Ultra-Soft Pseudo-Potentials [21] were used to emulate the effects of the core-electrons. The spin effects are considered for all the investigated systems by self-consistent spin-polarized calculations. The properties of the MgH<sub>2</sub> determined for the values of 380 and 500 eV for the energy cut-off are almost identical, but with an almost double computational effort for  $E_{\text{cut}} = 500$  eV. The Brillouin zone is discretized with a spacing



**Fig. 1** – The illustration of the elementary cells used in the present study: (a) the primitive cell of the  $\beta$ -MgH<sub>2</sub>. (b) The structure of the supercell ( $\sqrt{2} \times \sqrt{2}$ )R45° × 2 used for the study of the doping of the bulk magnesium hydride; the first digit of the atom index indicates the layer where the atom is located, (c) the slab model of the magnesium hydride surface (001). The green balls represent the magnesium atoms, the white balls the hydrogen atoms and the red balls indicate the substitution position. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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