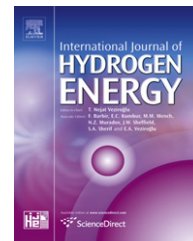


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# Electronic and bonding properties of MgH<sub>2</sub>–Nb containing vacancies

C.R. Luna<sup>a</sup>, C.E. Macchi<sup>b,\*</sup>, A. Juan<sup>c</sup>, A. Somoza<sup>d</sup>

<sup>a</sup> IFIMAT, UNCentro and ANPCYT, Pinto 399, B7000GHG Tandil, Argentina

<sup>b</sup> IFIMAT, UNCentro and CONICET, Pinto 399, B7000GHG Tandil, Argentina

<sup>c</sup> Dpto. Física, Universidad Nacional del Sur, Av. Alem 1253, Bahía Blanca, Argentina

<sup>d</sup> IFIMAT, UNCentro and CICPBA, Pinto 399, B7000GHG Tandil, Argentina

## ARTICLE INFO

### Article history:

Received 25 June 2010

Received in revised form

25 August 2010

Accepted 26 August 2010

Available online 21 September 2010

### Keywords:

Magnesium hydride

First principle calculations

Electronic structure

Vacancies

## ABSTRACT

The magnesium hydride stability and bonding have been studied using density functional theory (DFT). To this aim, calculations on the electronic structure were performed. We also modeled the bulk hydride with a Nb atom as a substitutional impurity. Furthermore, both systems were modeled containing different types of vacancies (Mg, H or H–Mg complex). The crystal orbital overlap population for both the metal–metal and metal–hydrogen bonds was also computed. The influence of vacancy-like defects was studied through the calculation of the positron lifetimes in defected MgH<sub>2</sub> and defected MgH<sub>2</sub>–Nb. For the pure hydride, the results show an increment in the atom bonds in correlation with an increase of the positron localization reflected in a rise of the positron lifetimes. On the other hand, in all considered cases for Mg or/and H vacancies, the presence of Nb reduces the hydride bond about 36%. This decrease in the hydride stability was associated with a decrease in the probability of the positron localization and a consequently reduction of the positron lifetimes.

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## 1. Introduction

It is well known that the use of fossil fuels produces environmental compromise, the CO<sub>2</sub> emission contributes to global warming and the availability of oil reserves around the globe is related to geopolitical tensions. These issues stimulate the study of renewable and clean energy sources to replace the use of fossil fuels [1–3]. Hydrogen is a suitable energy vector to be used for the new economy. However, there are several technological problems that need to be solved, among them hydrogen storage on solid-state materials that chemically bind or physically absorb hydrogen at densities greater than the liquid phase [4]. Among light metals, magnesium hydride is considered one of the most promising

candidates for the reversible hydrogen storage due to its low price and high weight percent storage (7.6 wt.%). However, its slow hydrogenation and de-hydrogenation kinetics and the requirement of high temperatures (~300 °C) for its decomposition are the major shortcomings for mobile applications. To solve this problem, it has been proposed to dope MgH<sub>2</sub> with transition metals (TM), such as Nb, Sc, Ti, V, Y and Zr. Specifically, the transition metals act as catalysts reducing the desorption temperature [5–8]. In fact, understanding the microscopic mechanisms linked to the hydrogenation and de-hydrogenation processes are of utmost importance for industrial applications.

There is an interesting number of experimental and theoretical studies considering MgH<sub>2</sub> and MgH<sub>2</sub>–Nb [5–16]. Song

\* Corresponding author. Tel.: +54 2293 439670; fax: +54 2293 439679.

E-mail address: [cmacchi@exa.unicen.edu.ar](mailto:cmacchi@exa.unicen.edu.ar) (C.E. Macchi).

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doi:10.1016/j.ijhydene.2010.08.111

et al. [10] studied the influence of the doping elements on the  $\text{MgH}_2$  stability. These authors found a decrease in the heat of the  $\text{MgH}_2\text{-X}$  formation being  $X = \text{Cu, Ni, Al, Nb, and Fe to Ti}$ . This destabilization was attributed to a weakening of the  $\text{Mg-H}$  bonding. On the other hand, Xiao et al. [14] reported a decrease in the formation enthalpy of  $\text{MgH}_2\text{-TM}$ . They also analyzed the structural and electronic effects on these hydrides.

As known the diffusion in solids is mediated by vacancy-like defects. Specifically, the microscopic mechanisms operating in the hydrogenation and de-hydrogenation of magnesium hydride are related to the formation and diffusivity of vacancies in bulk  $\text{MgH}_2$  [17]. Therefore, it is essential to understand the role of the mentioned defects on the electronic and bonding properties. The H vacancy interaction metal has been the objective of several studies [18–21]. Under this frame, the aim of the present work is to study the metal–hydrogen bonding and the effect of the transition metals on the stability of the vacancy–hydride complexes in  $\text{MgH}_2\text{-Nb}$  using first principle calculations. Thus, after generating the crystal structure described in Section 3, *ab initio* calculations were performed to provide information on the energy and electronic structure of the hydrides pure and Nb doped  $\text{MgH}_2$ , and both structures containing vacancies.

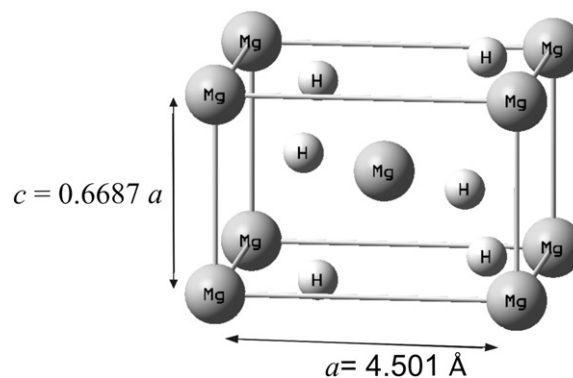
Positron annihilation spectroscopy, mainly positron lifetime technique (PALS) is almost the unique experimental tool to directly obtain information on vacancy-like defects (see a review in Ref. [22]). However, experimental studies on vacancy-like defects in magnesium hydrides are scarce [23–25], any contribution to this issue is of utmost importance. For example, there are no reported theoretical studies. In such a way, the present work is also addressed to the analysis of the structural changes in the hydrides in presence of point defects.

## 2. Computational method

The energy and electronic structure calculations for the absorption of hydrogen in  $\text{Mg-Nb}$  were carried out using two computational methods. The first, the atomic superposition and electron delocalization tight-binding (ASED-TB) formalism [26–28], implemented with the YAeHMOP package [29] is described in detail in Refs. [30–32]. Although the method is approximate, it has been used in the present work because it gives a starting point of the main interactions during the absorption process. In fact, the ASED-TB scheme has been successfully used as a comparative tool to study surface and interfacial phenomena in different metals–H systems [33–42].

**Table 1 – Atomic parameters for ASED-TB calculation.**

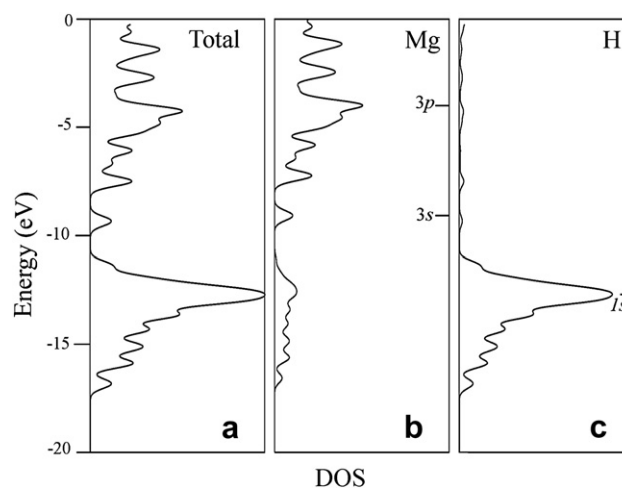
Atom	Orbital	IP (Ev)	$\xi_1$	$\xi_2$	$c_1$	$c_2$
H	1s	–13.6	1.3			
Mg	3s	–9.0	1.1			
	3p	–4.5	1.1			
Nb	5s	–10.10	1.89			
	5p	–6.86	1.85			
	4d	–12.1	4.08	1.64	0.6401	0.5516



**Fig. 1 – Unit cell of  $\text{MgH}_2$ .**

We used as input parameters, a basis set of atomic orbitals and experimental ionization potentials (IP). To obtain a detailed description of the electronic structure properties, we have used a full valence (*sp d*) set of Slater-type orbitals (STO). As usual, in the ASED approximation, single- $\zeta$  STO for the *s* and *p* orbitals and double- $\zeta$  STO for the *d* orbitals were used. The values of the Slater exponents applied were those optimized for Mg and Nb by Vela and Gázquez [43]. Regarding the experimental valence orbital IP values, which are used as the diagonal elements of the Hamiltonian matrix, spectroscopic data were utilized [44]. In order to minimize exaggerated electron drifts, the IP were adjusted following the same procedure reported in Ref. [45]. The atomic parameters are listed in Table 1.

Additional calculations were carried out within the gradient-corrected density functional theory (GC-DFT) using a supercell containing 48 atomic sites in a tetragonal lattice to model bulk  $\text{MgH}_2$  with a  $2 \times 2 \times 2$  reciprocal space grid in the supercell Brillouin zone. Specifically, we used the Amsterdam Density Functional 2000 package (ADF-BAND2000) [46]. The molecular orbitals were represented as linear combinations of Slater functions. The gradient correction of the Becke approximation for the exchange energy functional [47] and the B3LYP approximation for the correlation functional were



**Fig. 2 – (a) Total DOS curves for  $\text{MgH}_2$ , (b) Projected DOS in a Mg atom, (c) Projected DOS in an H atom. In (b) and (c) the corresponding atomic levels are labeled.  $E_F = -11.12 \text{ eV}$ .**

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