

## Hydrogen storage in $\text{MgH}_2$ matrices: A study of Mg-MgH<sub>2</sub> interface using CPMD code on ENEA-GRID

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(ricevuto il 22 Giugno 2009; pubblicato online il 9 Settembre 2009)

**Summary.** — The remarkable ability of magnesium to store significant quantities of hydrogen, in the form ( $\text{MgH}_2$ ), has fostered intense research efforts in the last years in view of its future applications where light and safe hydrogen-storage media are needed. However, further research is needed since Mg has a high operation temperature and slow absorption kinetics that prevent for the moment the use in practical applications. To improve and optimize the performances of this material a detailed knowledge of the hydrogen diffusion mechanism at the atomic level is needed. Experiments can only provide indirect evidences of the atomic rearrangement during the desorption process. For these reasons a detailed computational study of  $\text{MgH}_2$  is invoked to characterize the dynamics of hydrogen during desorption. Further insights are gained by characterizing the Mg-MgH<sub>2</sub> interface which is supposed to play a major role in the hydrogen diffusion during absorption and desorption cycles. By means of accurate *ab initio* molecular dynamics simulations based on the density-functional theory with norm-conserving pseudopotentials and plane-wave expansion (CPMD code) an interface is designed and studied. Extensive electronic structure calculations are used to characterize the equilibrium properties and the behavior of the surfaces in terms of total energy considerations and atomic diffusion.

PACS 07.05.Tp – Computer modeling and simulation.

PACS 61.50.Ah – Theory of crystal structure, crystal symmetry; calculations and modeling.

PACS 68.35.Fx – Diffusion; interface formation.

### 1. – Introduction

The development of a viable hydrogen storage system is becoming increasingly important for promoting the “hydrogen economy”. Several materials are good candidates for storing hydrogen, but, among them, magnesium hydride  $\text{MgH}_2$  is one of the most promising candidates as hydrogen storage media in automotive industry, due to its very high capacity (7.7 wt%), light weight and low cost of production. However, further research

is needed since Mg has a high operation temperature and slow absorption kinetics that prevent for the moment the use in practical applications. Experimentally, great efforts have been made to improve the H<sub>2</sub> absorption and desorption kinetics by mechanically milling MgH<sub>2</sub> with various additives [1-3]. However the atomic level mechanism by which hydrogen flows in and out of the hydride along the MgH<sub>2</sub>-Mg interfaces still remains unclear [4]. In order to have a better understanding of this mechanism, extensive *ab initio* molecular dynamics simulations have been performed to gain detailed information of the atomic level dynamics during desorption. Electronic structure calculations are used to determine the equilibrium properties and the behavior of the surfaces in terms of total energy considerations. Furthermore, the interface is studied at several values of the temperature, thereby characterizing the hydrogen atomic displacement.

## 2. – Computational details

We employed for all the calculations the CPMD (Car-Parrinello Molecular Dynamics) code [5,6]. CPMD is an *ab initio* electronic structure and Molecular Dynamics (MD) program using a plane-wave/pseudopotential implementation of density functional theory. Goedecker-Teter-Hutter pseudopotentials for magnesium and hydrogen, together with Padé approximant LDA exchange-correlation potentials were used [7]. The electronic wave functions are expanded in a plane-wave basis set with a kinetic energy cut-off equal to 80 Ry. The latter value was optimized by preliminary calculations both on simple molecules (Mg<sub>2</sub>, MgH and H<sub>2</sub>), and on the crystalline structures of metallic Mg and magnesium hydride. All the calculations were performed in the supercell approximation, in view of the large-scale molecular dynamics simulation of the interface, with periodic boundary conditions meant to mimic an infinitely extended system [8]. The crystal structure of Mg is the hexagonal close-packed and the crystal MgH<sub>2</sub> is considered in the  $\beta$ -MgH<sub>2</sub> atomic structure, TiO<sub>2</sub>-rutile type, that is observed at the atmospheric pressure and low temperatures [9].

## 3. – Model interface

A supercell approach is used to simulate the atomic system with the interface [10]. As shown in fig. 1, the Mg-MgH<sub>2</sub> interface is built by putting nearby two free surfaces obtained cutting both the Mg and MgH<sub>2</sub> crystals. The main constraint in building the interface is in the selection of two commensurate surfaces (one for Mg and one for MgH<sub>2</sub>) fulfilling a simulation cell with periodic boundary conditions (see fig. 1). Such a constraint narrows the possibilities of finding two suitable free surfaces for a proper interface. The interface considered in this work is the one composed by facing the (010) of Mg with the (110) of MgH<sub>2</sub>.

The Mg part is sketched in fig. 1a and the MgH<sub>2</sub> one in fig. 1b: these systems can interact through their internal free surfaces forming an interface as shown in fig. 1c (132 Mg atoms and 120 H atoms). Each free surface, selected according to periodic boundary conditions, is relaxed without taking into account any possible reconstruction upon changing the temperature. The total length of the system is  $L_y = 50.30 \text{ \AA}$ , while in the  $x$ - and  $z$ -direction the system has  $L_x = 6.21 \text{ \AA}$  and  $L_z = 15.09 \text{ \AA}$ , respectively. On both sides of the system, a void region of length  $2 \times L_x$  is considered to suppress the interaction, due to periodic boundary conditions, between the external surfaces of Mg and MgH<sub>2</sub> that are kept fixed. Zero-temperature total energy calculations are used to evaluate interface stability and MD simulations, at constant volume and constant

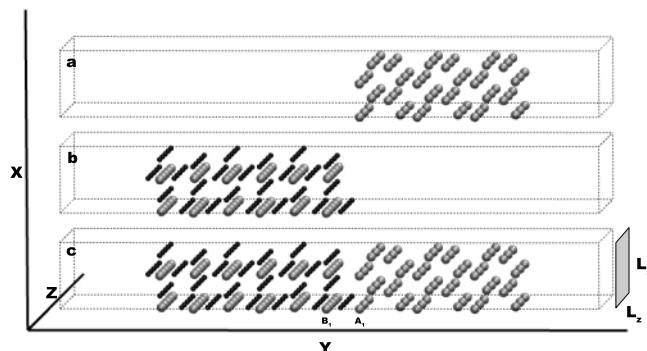


Fig. 1. – Simulation cell for first-principle molecular dynamics simulations: a) Mg bulk with the internal surface on the left; b) MgH<sub>2</sub> with the internal surface on the right; c) starting configuration of the Mg-MgH<sub>2</sub> interface.

temperature, are performed to characterize the hydrogen diffusion [10]. To understand the atomic level dynamics of hydrogen diffusion at the interface, MD simulations starting from room temperature ( $T = 300$  K) and up to  $T = 900$  K are performed. In this range of temperature, a phase transition from MgH<sub>2</sub> to Mg + H<sub>2</sub> is experimentally observed, accompanied by the desorption of hydrogen. Molecular dynamics simulations, performed from room temperature to 900 K, reveal an increased mobility of hydrogen atoms near the interface. Furthermore, diffusion of hydrogen atoms starts at  $T = 700$  K, in agreement with experimental observations, confirming the accurateness of the *ab initio* approach. The mobility of interface hydrogen is much higher than for bulk hydrogen atoms. This difference increases at higher temperatures and no hydrogen atoms are observed to diffuse in the Mg bulk.

#### 4. – Parallelization benchmark

We test the CPMD code for the system showed in fig. 1c representing a Mg-MgH<sub>2</sub> interface constituted by 132 atoms of magnesium and 120 atoms of hydrogen. We use a CPMD (version 3.11.1) code compiled with Intel Fortran Compiler (v10.1), MKL library and MPI parallelization on High-Performance Computer named CRESCO [11]. CRESCO is a TOP500 Computer ([www.top500.org](http://www.top500.org)) based on Intel Xeon Quad-Core microprocessors (each node is composed by 2 processors and 8 cores). In fig. 2 we show the speed-up calculated from the total time required by the code to perform 300 molecular dynamics time steps using an increasing number of cores (from 8 up to 576). The benchmark results demonstrate the high performance of the CPMD parallelization on CRESCO architecture and the good scalability up to hundreds of cores.

#### 5. – Conclusions

We have shown that *ab initio* electronic structure calculations are able to discover atomic level phenomena that are critical for the progress in a technologically relevant

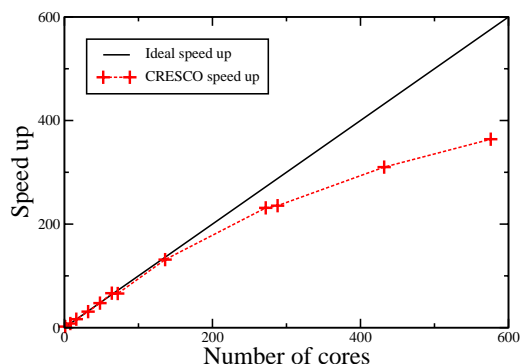


Fig. 2. – Speed-up of CPMD code *versus* number of cores in HPC CRESCO.

issue like the one related to the hydrogen storage. Moreover the availability of a high-performance computer allows an accurate simulation of the critical regions of the simulated system.

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The financial support from the Italian Ministry of research through the ENEA projects TEPSI and CRESCO is gratefully acknowledged. We would also thank drs. M. VITTORI ANTISARI, S. MIGLIORI and G. BRACCO for useful discussions.

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