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Ab initio study of MgH_2: Destabilizing effects of selective substitutions by transition metals

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ABSTRACT

The strong ionicity of H within rutile MgH_2 is reduced by selective substitution of Mg by T (=Fe, Co, Ni, Pd, Pt) using trirutile super-structure host TMg_2H_6. These novel model systems, as computed in the quantum mechanical framework of density functional theory, showed a gradual decrease of the charges carried by H down to $-0.02e$ improving the use of MgH_2 for applications.

1. Introduction

Hydrogen storage materials such as hydrides are leading candidates for clean energy in the future. Archetype hydride MgH_2 has been studied intensively owing to its large gravimetric density ~7.6 wt.%. However, its high thermodynamic stability prevents hydrogen absorption/desorption at mild conditions, whence the difficulty of its *ad hoc* use in applications. Experimental and theoretical efforts have culminated over decades to overcome the latter intricacy. The kinetics of hydrogenation were improved experimentally either by the addition of catalysts [1–3] or by the introduction of nickel as an adjoined metal such as in Mg_2NiH_4 [4]. Recent theoretical investigations suggested the insertion of light elements such as carbon and boron which decreased the largely ionic character of hydrogen in $(B,C)_{0.167}MgH_2$ [5].

The aim of the present study is to remedy the situation prohibiting the use of MgH_2 in devices by selective substitution of Mg with transition metals (T = Fe, Co, Ni, Pd, Pt) in a trirutile host super-structure using first-principles density functional theory (DFT) calculations [6,7].

2. Structural details

As illustrated in Fig. 1, ordered trirutile TMg_2H_6 crystallizes as rutile with the tetragonal structure in space group $P4_2/mnm$ (No. 136). Given in Wyckoff letter, T atoms occupy $2a$ sites at coordinates $(0, 0, 0)$, and Mg atoms are found in $4e$ sites at $(0, 0, z\text{~}1/3)$. There are two hydrogen sub-lattices, namely H1 at $4f\,(x, x, 0)$ and H2 at $8j\,(x, x, z)$. Both Mg and T species are surrounded by irregular H octahedra. Successive T–H planes (at $z = 0$ and $z = 1/2$) are separated by two Mg–H planes (at $z\text{~}1/6$ and $z\text{~}1/3$).

Archetype MgH_2 crystallizes with the tetragonal rutile structure in space group $P4_2/mnm$ (No. 136). The latter order can be compared to the trirutile structure by substituting T species by Mg at $2a$ sites, whereby H atoms are located exclusively at $4f$ sites.

3. Computational methodology

Geometry optimization and total energy calculations were performed with the Vienna ab initio simulation package (VASP) [8,9]. The ion–electron interactions were described using the projector augmented wave (PAW) method [9,10]. Electron exchange-correlation functionals were built within the generalized gradient approximation (GGA) scheme following the nonlocal correction of Perdew, Burke and Ernzerhof (PBE) [11]. It is important to mention that semi-core p states where accounted for PAW

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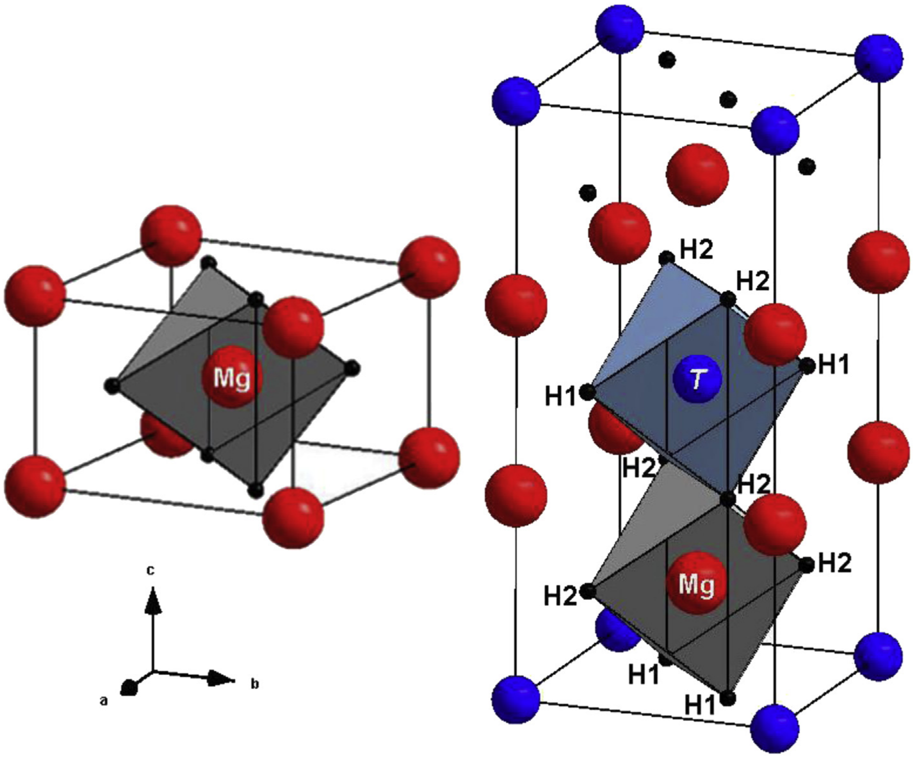

Fig. 1. Sketches of the crystal structures of rutile-type MgH_2 (left-hand side) and trirutile-type TMg_2H_6 (right-hand side).

potentials of Mg in order to obtain the correct physical bulk properties and electronic structures for TMg_2H_6 models. The conjugate-gradient algorithm [12] is used in this computational scheme to relax the atoms and to optimize the structural parameters until the forces on all the unconstrained atoms were less than 0.02 eV/Å and all stress components were less than 0.003 eV/Å^3. The tetrahedron method with Blöchl corrections [10] and a Methfessel–Paxton [13] Gaussian smearing scheme were applied for both geometry relaxation and to accelerate the total energy calculations. Brillouin-zone (BZ) integrals were approximated using the special *k*-point sampling. The calculations are converged at an energy cut-off of 404 eV for the plane-wave basis set with respect to the *k*-point integration with a starting mesh of 4 × 4 × 4 up to 8 × 8 × 8 for best convergence and relaxation to zero strains.

In this work, the atomic charge of hydrogen is calculated using a Bader charge analysis [14]. The latter approach partitions the continuous electron density into region bounded by the minima of the charge density. Such an analysis can be useful when trends between similar compounds are examined; it does not constitute a tool for evaluating absolute ionizations. Bader's analysis is done using a fast algorithm operating on a charge density grid [15]. The results of computed charges Q are such that they lead to neutrality when the respective multiplicities are accounted for.

4. Results and discussions

4.1. Geometry optimization, cohesive energies and hydrogen charge density

In as far as TMg_2H_6 models are novel theoretical models chosen herein, geometry optimization was firstly performed. Starting and optimized structural parameters are given in Table 1. Rutile-type MgH_2 was also examined to establish trends of stability for the computed TMg_2H_6 models. The calculated structural parameters for MgH_2 are within 2% of the experiment. All TMg_2H_6 models relaxed in the trirutile structure. The stability of these models can be examined from the computed total electronic energies given in Table 2.

The cohesive energies of various TMg_2H_6 structures were calculated with the expression.

$$E_{\mathrm{coh.}} = E(T_2Mg_4H_{12}) - 2E(\mathrm{T}) - 4E(\mathrm{Mg}) - 6E(\mathrm{H}_2)$$

The energy terms on the right-hand side of the equation represent, in order, trirutile hydride model, pure *T* metal, pure Mg, and gas-phase hydrogen. The strength of cohesive energy of a model is a measure of the stability of that model. Largely negative $E_{\mathrm{coh.}}$ indicate stable binding, whereas positive energies correspond to an unstable model. The energy of the gas-phase hydrogen dimer was calculated with an 8 × 8 × 8 cell. The cohesive energy per H_2 of MgH_2 is calculated within 8% of the experimental value −0.79 eV [16]. The computed $E_{\mathrm{coh.}}$ per H_2 values in Table 2 clearly indicate that all TMg_2H_6 models are stable owing to the negative values. Compared to MgH_2, all models are less stable. The latter finding meets with the aims of this study in as far as less thermodynamically stable hydrides are sought.

The latter should be comforted further by examining the atomic charge of hydrogen shown as a function of *T* species in Fig. 2. As expected, hydrogen exhibits a less ionic character near *T* elements (H1 sub-lattice) compared to H charges near Mg (H2 sub-lattice). This can be explained by the electronegativity value of the different species given in the Pauling scale: $\chi(\mathrm{Mg}) = 1.31$, $\chi(\mathrm{Fe}) = 1.83$, $\chi(\mathrm{Co}) = 1.88$, $\chi(\mathrm{Ni}) = 1.91$, $\chi(\mathrm{Pd}) = 2.2$, and $\chi(\mathrm{Pt}) = 2.28$. All *T* elements are more electronegative than Mg, whence the less ionic hydrogen in their surroundings. Furthermore, H1 charge near *T* elements undergoes gradual reduction of its ionic character from $H^{-0.4}$ for $FeMg_2H_6$ model down to $H^{-0.02}$ for $PtMg_2H_6$. The latter value is also due to the large H1-Pt separation $d_{\mathrm{H1\text{-}Pt}} = 1.80$ Å. The other hydrogen sub-lattice, namely H2, exhibits a constant evolution around a charge of -6*e*. Nevertheless the