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CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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DFT study of MgH₂ and AlH₃ hydrides doped with 3d transition metals

DFT studija MgH₂ i AlH₃ hidrida dopiranih 3d prelaznim metalima

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Abstract

The electronic structures of lightweight binary hydrides MgH₂ and AlH₃ doped with 3d transition metals (TM=Sc, Ti, Mn, and Cu) were investigated using first-principles calculations. The influence of 3d states of TM was clearly visible from electronic structure calculations. Doping of these systems has a favorable influence on hydrogen desorption energies of both systems, decreasing it in the case of MgH₂ for all TM and increasing it in metastable AlH₃ when doped with Sc and Ti.

Keywords: MgH₂; AlH₃; transition metal substitution; DFT; Hydrogen energy storage.

Izvod

Elektronske strukture lakih binarnih hidrida MgH₂ i AlH₃ dopiranih 3d prelaznim metalima (PM=Sc, Ti, Mn i Cu) su ispitane primenom proračuna iz prvih principa. Na osnovu proračuna elektronske strukture jasno je vidljiv uticaj 3d stanja PM. Dopiranje ovih sistema ima povoljan uticaj na energije desorpcije vodonika oba sistema, smanjujući je u slučaju MgH₂ za sve PM i povećavajući je u metastabilnom AlH₃ kada se dopira sa Sc i Ti.

Ključne reči: MgH₂; AlH₃; Supstitucija prelaznim metalom; DFT; Skladištenje energije vodonika.

Introduction

Hydrogen has been recognized to have a large potential to be used as a fuel or energy vector. The first step for its practical application is its safe and efficient production and storage. Metal hydrides represent perspective systems for solid state hydrogen energy storage materials [1].

Lightweight binary hydrides MgH₂ and AlH₃, which are the subjects of research in this paper, have high volumetric hydrogen density (110 and 148 g H₂/L, respectively) and a gravimetric hydrogen density that exceeds 7.6% and 10 wt.%, respectively [2, 3]. Employing these systems as successful hydrogen storage materials is still hindered by obstacles concerning hydrogen adsorption/desorption kinetics, cycle life, and reaction thermodynamics of potential material candidates. Several different methods, i.e. nanostructuring by mechanical milling, the addition of transition metals (TM), their oxides and intermetallics can improve thermodynamic and kinetic properties [2, 4, 5]. This paper examines the influence of 3d transition metal substitution in MgH₂ and AlH₃ host matrix through results obtained from electronic structure calculations.

MgH₂ is a stable binary hydride with a rutile crystal structure with high hydrogen desorption temperature (447°C) and slow desorption kinetics. Doping of this hydride with transition metals was extensively studied by many authors [6-8] and a lowering of stability was reported. On the other hand,

α -AlH₃ is metastable at room temperature although the most stable among 8 different polymorphs that exist. In single-step reaction, it releases hydrogen at lower temperatures <100°C but the opposite direction – rehydrogenation is not possible under the same conditions. There are a few studies concerning investigations of the influence of dopants on stability and enhancement of some aspects of AlH₃ [9-11]. In this paper, we have selected to examine transition metals from the beginning (Sc, Ti), middle (Mn) and end of the 3d group (Cu), so we can trace impact of partially filled to almost filled 3d orbitals of TM on MgH₂ and AlH₃ host matrix.

Methods and calculation parameters

The calculations for pure MgH₂ (space group 136: P4₂/mnm) and its doped systems were performed using the full potential (linearized) augmented plane waves method with the addition of local orbitals (FP-LAPW+LO) implemented in WIEN2k software package [12]. RMTKmax parameter, which defines the size and completeness of the (L)APW basis set, is chosen to be 7.0 in all cases. The radii of MT-spheres were set to 1.6 bohr for all atoms. The exchange-correlation effects were included within the generalized gradient approximation (GGA). The supercell was constructed from 8 rutile MgH₂ unit cells in the 2x2x2 arrangement having 48 atoms in the primitive cell with one of the 16 Mg atoms substituted with a TM atom (see Fig. 1).

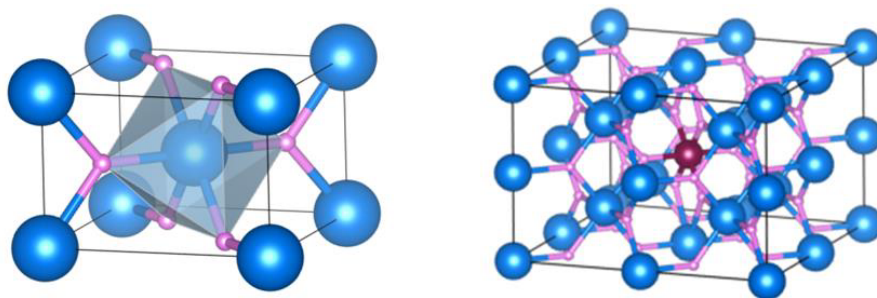


Figure 1. MgH₂ unit cell (left) and primitive 2x2x2 supercell of MgH₂:TM systems (right). Small pink spheres - H, blue spheres - Mg, maroon sphere - TM.

Initial parameters for the supercell were obtained after full optimization of rutile MgH₂ unit cell parameters. After the substitution of the Mg atom by TM, relaxation of the structure has been performed by minimizing the forces acting on atoms while keeping the cell parameters fixed. The Brillouin zone sampling was performed using k points in the 3x3x4 arrangement.

The same method discussed previously was used to study the AlH₃ α -polymorph (space group 167: R-3C) and its electronic structure, adjusting the choice of parameters. The parameter RMTKmax was set to 5.00 while the radii of MT-spheres for Al and H were 1.75 bohr and 0.95 bohr, respectively. The sampling of the Brillouin zone was done using a 14×14×14 grid. To study TM substituted systems, supercells were constructed from AlH₃ unit cells in a 2x2x1 arrangement consisting of 96 atoms, with one of the 24 Al atoms replaced by a TM (see Fig. 2).

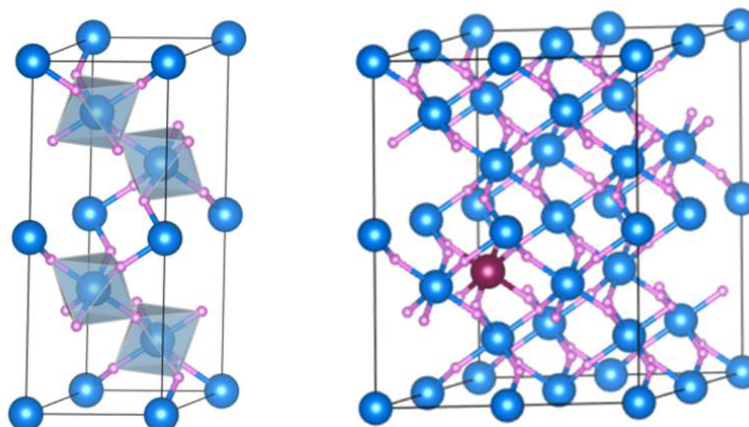


Figure 2. AlH_3 unit cell (left) and primitive $2 \times 2 \times 1$ supercell of $AlH_3:TM$ systems (right). Small pink spheres - H, blue spheres - Al, maroon sphere - TM.

Due to the large number of atoms in the TM substitution of Al in α - AlH_3 systems, the investigation was done using the program package Quantum ESPRESSO [13]. The choice of this program package considerably reduced computational time for these systems retaining obtained accuracy from previously used software for calculations. Exchange-correlation interactions were treated by GGA of Perdew and Wang (PW91). The Kohn-Sham electronic orbitals are expanded on a plane-wave basis and set up to a kinetic energy cutoff of 37 Ry. The k-point sampling integration over the Brillouin zone is estimated using a $2 \times 2 \times 1$ arrangement. Full relaxation of the pure AlH_3 and subsequent relaxation of the nearest dopant environment is done.

Results and discussion

Details of the electronic structure are presented through calculated total and atomic projected densities of states for pure MgH_2 and doped systems in Fig. 4. The first coordination of Mg atom consists of 6 H atoms that form octahedron, four are coplanar H atoms (denoted as H4) and two occupy remaining vertices (denoted as H2).

The most pronounced difference between pure and doped MgH_2 systems stems from narrow, well localized 3d states of the TM impurity. Going from the beginning to the end of the TM series, the charge increases from Sc to Cu, and 3d states shift towards lower energies together with the Fermi level [14]. From the bottom of the conduction band for the nearly empty band of Sc, states shift down to the energy gap for Ti and Mn, and reach the top of the valence band for the almost fully occupied bands of Cu. For Ti, Mn, and Cu two groups of peaks appear indicating crystal field splitting of their 3d states in an octahedral environment of H atoms. In the case of Cu impurity 3d state spreads over a broader energy range in the valence band and the localized peak of hybridized 3d state reaches the top of the valence band. The effects of hybridization and interaction of TM 3d states with the states of surrounding H atoms are visible in the valence band and the gap.

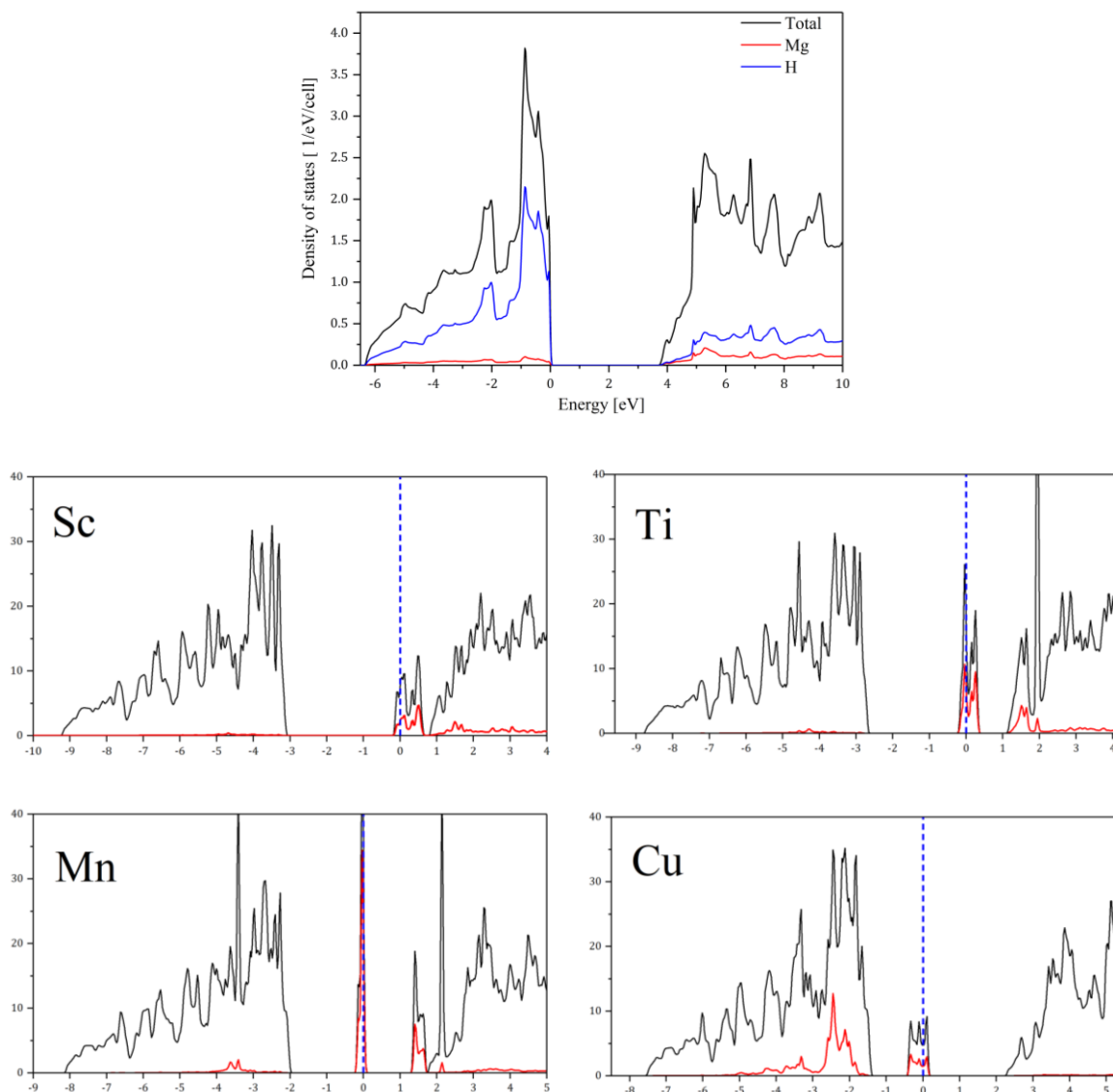


Figure 3. (top) Total and atomic densities (Mg – blue and H-red) of states of MgH_2 . (bottom) Total (black) and TM projected (red) densities of states of $\text{MgH}_2\text{:TM}$ (TM= Sc, Ti, Mn, Cu). Fermi level is denoted with (blue) dashed vertical line.

From these results, it is clear that TM impurities make an impact on the MgH_2 host matrix that can be observed on an electronic level (Fig. 3) and verified by calculated hydrogen desorption energies for these systems. The system for practical use as a hydrogen storage medium should have an enthalpy of formation between 20-50 kJ/mol H_2 [15] to easily release H_2 . In Table 1. desorption energies of pure MgH_2 and doped systems are presented. The observed values indicate that by inserting TM impurity, desorption energies decrease from Sc to Cu. Also, distances between TM and H atoms decrease, except Sc, leading to the assumption that TM from Ti to Cu bond stronger with H atoms from the first coordination and weaken the rest of the MgH_2 matrix.

Table 1. The shortest distances of Mg/TM from H atoms in the first coordination, total electronic energies, and dehydrogenation energies of pure and doped MgH₂. The grey fields refer to the MgH₂ compound, so the corresponding values are the Mg-H₂ and Mg-H₄ distances. *Experimental values [16]. **Experimental value [17].

TM	TM-H ₂ [Å]	TM-H ₄ [Å]	E[Ryd]	ΔE^{deh} [kJ/molH ₂]
Mg	1.959 1.979*	1.944 1.980*	-403.037	71.98 74.06**
Sc	2.013	2.023	-7576.417	70.56
Ti	1.920	1.931	-7755.504	61.88
Mn	1.732	1.727	-8365.082	54.13
Cu	1.781	1.888	-9357.792	51.72

In Fig.4, densities of states for pure and doped AlH₃ are presented. 3d states of TM are present in the valence and conduction band and follow the same trend as in the case of MgH₂. The impact of the TM doping on AlH₃ is also verified in Table 2. by the values of calculated hydrogen desorption energies [18]. In the case of AlH₃ enthalpy of formation is too low, expressing the fact that this is a metastable system. Therefore doping with Sc and Ti rise stability is a favorable route to approach the range of stability for practical application.

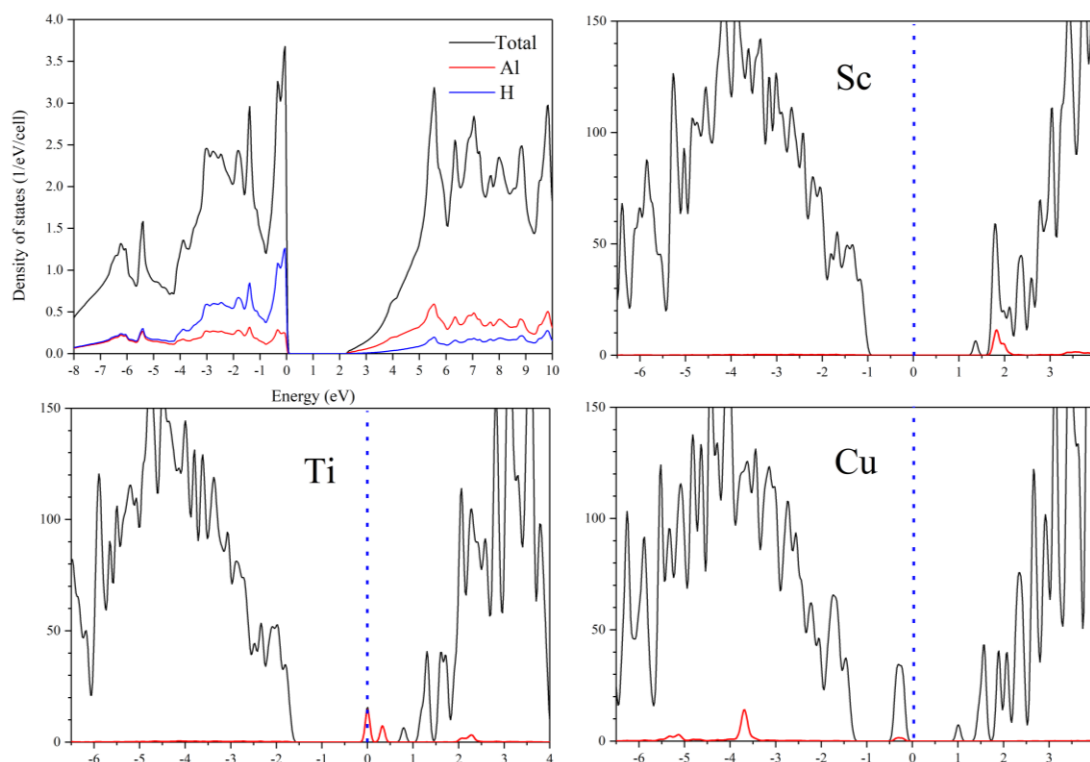


Figure 4. (top-left) Total and atomic densities (Al – blue and H – red) of states of AlH₃. (top-right and bottom) Total (black) and TM projected (red) densities of states of AlH₃:TM (TM = Sc, Ti, Cu). Fermi level is denoted with (blue) dashed vertical line.

Table 2. The shortest distances of Al/TM from H atoms in the first coordination, total electronic energies, and dehydrogenation energies of pure and doped AlH₃. The grey fields refer to the AlH₃ compound, so the corresponding values are the Al-H distances. *Experimental values [19]. **Experimental value [20].

TM	TM-H[Å]	E[Ryd]	ΔE^{deh} [kJ/molH ₂]
Al*	1.717 1.715*	-489.1444	7.6 7.9**
Sc	1.858	-	14.8
Ti	1.804	-	12.3
Cu	1.646	-	1.4

It can be noted that TM-H distances increase for Sc and Ti-doped systems compared to the pure one, along with hydrogen desorption energy. In the case of Cu, desorption energy is even less than in pure AlH₃, so its influence is not beneficial to the system.

Conclusion

In this paper, we have observed the influence on the stability of 3d transition metal on binary hydrides MgH₂ and AlH₃. Our results obtained from electronic structure calculations imply that doping MgH₂ with TM decreases the stability of this system, making it more suitable for the hydrogen storage medium. Also, when doping AlH₃ with Sc and Ti, desorption energies increase. From these considerations, although these hydrides are opposite cases, doping with 3d transition metals brings them closer to achieving at least condition regarding stability when employing them as hydrogen storage materials.

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