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Transition metal doping of Mg_2FeH_6 – an DFT insight into synthesis and electronic structure

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Abstract

Mg_2FeH_6 is a promising hydrogen storage material with volumetric hydrogen density among the highest known. However, its complicated synthesis and high temperature of hydrogen desorption limit wider applications. In this paper we study the influence of transition metal (Ni, Co, Mn) doping on the structural, electronic and hydrogen sorption properties of Mg_2FeH_6, using first-principles density functional theory calculations. The thermodynamics of three different synthesis routes is addressed, and all of the mentioned transition metals are found to destabilize Mg_2FeH_6. In addition, a detailed study of electronic structure properties, including densities of states (DOS) and charge transfer analysis (AIM), reveals that the doping with Ni, Mn and Co leads to the reduction of the direct gap of Mg_2FeH_6.

Key words: Mg_2FeH_6, DFT, transition metals, electronic structure

1. Introduction

Mg-based transition-metal complex hydrides, such as Mg_2NiH_4, Mg_2CoH_5 and Mg_2FeH_6, are extensively investigated for the hydrogen storage applications[1,2,3,4]. They consist of a transition metal (TM) covalently bonded to the hydride ligands to form a complex anion $[TMH_x]^{\delta-}$ which is stabilized by Mg^{2+} cations[5]. Although this class of metal hydrides has lower gravimetric hydrogen capacity as compared to pure magnesium hydride (7.6 wt % for β-MgH_2, 5.5 wt % for Mg_2FeH_6), it is still very attractive due to the large volumetric capacities[6].

Mg_2FeH_6, with volumetric capacity of 150 gdm^{-3} (more than twice that of liquid hydrogen), has one of the highest known hydrogen densities among the hydrogen storage materials investigated so far[1]. Different values for the experimentally measured heat of Mg_2FeH_6 formation exist in the literature (-98 ± 3 $kJmol^{-1}H_2$[7], -80 ± 7 $kJmol^{-1}H_2$[8], $-67.2 \pm 8 kJmol^{-1}H_2$[9]), but the overall consensus is that its stability does not differ significantly from that of β-MgH_2 (-74.4 $kJmol^{-1}H_2$[10]). However, the catalytic role of iron, or other TM in the case of quaternary hydrides, has proven to be an important factor in the improvement of hydrogen sorption kinetics[2,11]. Given all the characteristics, Mg_2FeH_6 is considered as highly suitable material for the thermochemical energy storage, such as storage of solar or excess industrial heat[6], and numerous researches are done in order to optimize the synthesis and study or predict the properties of Mg_2FeH_6 and Mg_2FeH_6-based mixed complex hydrides. Also, Mg–TM-hydrides are investigated as prosperous third generation switchable mirrors, given they can change reversibly from a metallic to a transparent state upon hydrogen absorption[12,13].

Opposed to the Mg_2NiH_4, that can be formed by hydrogen absorption in the intermetallic compound Mg_2Ni, synthesis of Mg_2CoH_5 and Mg_2FeH_6 must be achieved in other ways, since the starting binary alloy is not experimentally synthesized. Mg_2FeH_6 was first produced by sintering elemental powders at both high temperature and high hydrogen pressure[7]. High proportion of nanocrystalline Mg_2FeH_6 was also recently obtained by ball milling of 3Mg+Fe mixture under relatively lower hydrogen pressure at room temperature[9]. First direct synthesis was achieved by ball milling of $2MgH_2$ + Fe mixture in a reactive H_2 atmosphere, according to the chemical reaction[14]: $2MgH_2 + Fe (+H_2) \rightarrow Mg_2FeH_6$. Similar reaction is suggested for the rehydrogenation of Mg_2FeH_6[15]. Ever since, reactive ball milling of Mg and Fe or MgH_2 and Fe mixtures under different hydrogen pressure and temperatures has been used as a way of producing Mg_2FeH_6 or corresponding quaternary complex hydrides[11,3,16,17,9,18,19]. It was shown that, regardless of the use of metallic magnesium or MgH_2 powder with iron, MgH_2 forms prior to Mg_2FeH_6 both after cycling and during absorption at higher hydrogen pressures[20,21]. Therefore, the following reaction is suggested for the formation of Mg_2FeH_6 phase: $3MgH_2 + Fe \rightarrow Mg_2FeH_6 + Mg$[20,21]. When the formation of MgH_2 is both kinetically and thermodynamically favored, MgH_2 acts as a competitor to the formation of the ternary hydride, while at sufficiently low pressures (below 5 bar) direct formation of Mg_2FeH_6 is more thermodynamically favorable[2]. However, in the case of mixed transition-metal complex hydride, some other mechanisms have been suggested. For $Mg_2(FeH_6)_{0.5}(CoH_5)_{0.5}$, it was suggested that the H-absorption occurs fairly quickly at the Mg/Fe–Co interface, and that complex hydride is formed directly from the elements via interface-controlled growth processes[2]. First principles calculations in combination with experimental techniques suggest formation of MgH_2 and (Mg,Fe) solid solution prior to Mg_2FeH_6[6].

Regarding hydrogen desorption, experiments so far suggest that Mg_2FeH_6 decomposes directly to the elemental Mg and Fe according to the reaction[2,15]: $Mg_2FeH_6 \rightarrow 2Mg + Fe + 3H_2$, without formation of MgH_2 as an intermediate phase[15]. A similar result was found by Gennari et al.[17] and Bogdanović et al.[22]

In this paper we study the role of substitution of iron by other transition metals in Mg_2FeH_6 by means of DFT (Density Functional Theory) calculations. The thermodynamics of hydride formation, regarding all mechanisms proposed in literature, as well as hydrogen desorption, is studied in order to predict the properties of quaternary hydrides and trends in their hydrogen storage properties. Also, the electronic structure and bonding are systematically investigated to reveal trends after the partial substitution of iron by Mn, Ni or Co in Mg_2FeH_6.

2. Details of calculations:

The unit cells of studied systems are shown in Fig.1. Mg_2FeH_6 has a K_2PtCl_6-type cubic structure (space group of Fm-3m) composed of tetrahedral sites of Mg^{2+} ions and octahedral $(FeH_6)^{4-}$ complexes[2], Fig.1a. To model the substitution of iron by other metals, one of the four equivalent Fe atoms in the unit cell of Mg_2FeH_6 was replaced by, subsequently, Mn, Ni and Co, resulting in hydrides with structural formula $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Ni,Co), Fig.1b.

The band structure calculations were performed using a Full Potential (Linearized) Augmented Plane-Waves plus local orbitals (FP (L)APW + lo) method[23], as implemented in Wien2k[24] program package based on the density functional theory[25]. The exchange and correlation effects were included within the generalized gradient approximation, using the Perdew–Burke–Ernzerhof scheme[26]. The radii of the muffin-tin (MT), non-overlapping spheres centered at the atomic nucleus, R_{mt}, were 2.0 bohr for Mg, 1.8 bohr for Mn,Fe,Co and Ni, and 0.8 bohr for H. Mixed LAPW/APW+lo basis set was used, while the energy to separate core and valence states was -6Ry. The parameter that determines the number of basis functions used in the calculation, $R_{mt}K_{max}$, was set to 5. The core states were treated fully relativistically, while the valence states were treated within the scalar relativistic approximation. Inside the MT spheres the wave functions were expanded in spherical harmonics up to l_{max}=10, and the charge density was Fourier expanded up to G_{max}= 20Ry. The Brillouin zone integration was achieved via a tetrahedron method[27], using a mesh of 286 irreducible k-points. Self-consistency was achieved by demanding that the convergence of the integrated charge difference between the two successive iterations was less than 10^{-5} electrons. The unit cell volumes were optimized, and the investigated structures were relaxed until the forces acting on all atoms were less than 1 mRy/bohr.

Additionally, the vibrational frequencies and zero point energy (ZPE) for the investigated compounds were calculated with the Vienna Ab initio Simulation Package (VASP)[28]. Using the Hessian matrix created from the finite differences method with displacements of 0.04 Å, we obtained the vibrational modes at Γ-point, which were then used to calculate the ZPE of the hydrides.

The enthalpies of hydride formation at 0K according to the different mechanisms of hydride formation were calculated by determining the energy difference between total calculated energy of the studied hydrides and total energy calculated for the reactants: metals, MgH_2 and molecular hydrogen; more details about these calculations can be found in our previous work[29].

3. Results:

3.1. Thermodynamics of hydride formation

The optimized structural parameters and calculated total energy of Mg_2FeH_6 and $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Ni,Co) are presented in Table 1. The optimized lattice constant of Mg_2FeH_6 differs by 0.4% from the available experimental value, Table 1. Based on the optimized structures of quaternary hydrides, it is shown how replacement of quarter of Fe atoms by Mn, Co and Ni atoms leads to a small increase of the unit cell volume and Mg-H distance.

Calculated energy changes for all investigated hydrides, i.e., the contributions of zero point energy (ΔE_{zpe}) and electronic energy change (ΔE_{el}) to the total energy change($\Delta E = \Delta E_{zpe} + \Delta E_{el}$), for different synthesis routes are presented in Table 2. Given that the decomposition reactions, or one step of these reactions($\Delta E_{des} = -\Delta E$), for all studied hydrides can be viewed as reversed to the synthesis reactions, in Fig.2 total energy change for desorption according to this 3 reaction mechanisms is presented.

Since the calculated total energy change can be viewed as approximation of the enthalpy change for the hydride formation reaction[30,31], from the results obtained for 3 different synthesis paths (Table 2) some conclusions can be drawn regarding thermodynamics of hydride formation. The smallest energy change is related to the reaction of MgH_2 transformation into complex hydride (reaction 2), while the most excessive energy is related to the process of direct synthesis (reaction 3). This conclusion holds for all of the studied hydrides. Good agreement is found between the total energy change for Mg_2FeH_6 formation directly from metals and molecular hydrogen (-39.4 $kJmol^{-1}H$, Table 2) and the enthalpies reported in the literature for the same reaction: - 40 $kJmol^{-1}H$[8], - 49 $kJmol^{-1}H$[7]. Also, there is a good agreement with the enthalpy (-42.20 $kJmol^{-1}H$) calculated in an earlier LAPW study[32]. The calculated energy changes can assist the analysis of experimental results; for example, given that the synthesis route shows significantly lower enthalpies of formation than the ones predicted (e.g. the one reported for the synthesis of the nanostructured Mg_2FeH_6[9]) other mechanisms are expected to be favored over direct synthesis.

The effect of transition metal doping would be significant in the case of direct decomposition of hydrides, reaction 3, Fig 2. The largest decrease of desorption enthalpy, expected in the case of nickel doping for the studied systems, would imply that 27.7 $kJmol^{-1}H$ energy change is required for hydrogen desorption. This is significantly lower than the experimental value for MgH_2 desorption enthalpy, 37.2 $kJmol^{-1}H$[10], and close to the values for several metal hydrides[33,34,35]. Still, having in mind that 19.8 $kJmol^{-1}H$ is needed for near-ambient storage applications[36], it seems that other modifications besides composition variations are required to bring Mg_2FeH_6 closer to this type of applications. However, if decomposition is to follow any other mechanism that would proceed through MgH_2 as intermediate state, the thermodynamic stability of MgH_2 would limit the doping influence and a significant decrease of desorption temperature could not be expected. For example, significant influence of transition metal doping is observed also for two other studied decomposition reactions, Fig.2, but both these reactions can be considered just as starting reactions of the more complex desorption mechanism that involves decomposition of MgH_2.

Based on the results of FP LAPW calculations, Shelyapina et al. found that the substitution of one half of cobalt atoms in Mg_2CoH_5 with iron atoms stabilizes the hydride[37]. This is in agreement with our results regarding the stability of $Mg_2Fe_{3/4}Co_{1/4}H_6$ as compared to Mg_2FeH_6, Table 2. Earlier study of transition metal doping in the case of Mg_2NiH_4 showed that Co stabilizes the hydrides, while Fe has a destabilizing effect[38], taking the stability of the staring metal alloys as the reference point. In the present study such comparison of the stability of doped systems vs. the stability of starting alloys would be meaningless since Mg_2Fe is not a stable alloy and, to the best of our knowledge, neither is $Mg_2Fe_{1-x}Ni_x$. We find that alloying with nickel would have the largest destabilizing effect on Mg_2FeH_6, leading to a quaternary hydride less stabile than Mg_2NiH_4 (- 32kJ/molH[39,40]), which is in agreement with earlier ab initio investigations[41,42]. Nevertheless, we believe that additional investigation of various nickel containing quaternary hydrides is needed to both clarify some opposite experimental findings[40], and consider the formation of stable Mg_2Ni alloy[38], that would lead to different desorption mechanisms than the ones proposed for Mg_2FeH_6.

From the results presented in Fig.2, conclusion can be drawn that, regardless of the synthesis route, we obtain the same trend in the stability of the studied hydrides. Namely, partial substitution of Fe by Mn, Co and Ni destabilizes the hydride, and the largest destabilization effect is expected in the case of alloying with nickel. Beside the nature of dopant, the doping concentration is also expected to play an important role. The results obtained in our study, compared with earlier studies of quaternary hydrides with different concentration of dopants[39,40,43], confirm present opinion in the literature that the hydrogen storage properties can be tailored by varying the relative content of the complex anion[16], since the stability of quaternary hydrides is in between the stabilities of the ternary complex hydrides. Exceptions to the expected stability are sometimes found in the nickel-doped system, as discussed above. The contribution of zero point energy change to the total energy change is the same for all hydrides in the same synthesis reaction. This is in agreement with the generally accepted assumption that the type of hydrogen position in the crystal lattice dominantly determines this contribution to the total energy change[38].

3.2. Electronic structure and bonding

To analyze how partial substitution of iron by other transition metals can be used to tune the hydride optical properties, we investigate the influence of metal doping to the electronic structure of Mg_2FeH_6. The total density of states (DOS), along with the relevant partial atomic contributions for all studied hydrides, is presented in Fig.3. The electronic structure of Mg_2FeH_6 is in agreement with earlier reports[6,37], showing that this hydride is semiconductor. The calculated width of the band gap is 1.85eV, which is in an excellent agreement with the results from other calculations[32,44], while to the best of our knowledge experimental value of band gap is not reported. Partial substitution of iron with other metals leads to the changes of electronic structure, as shown in Fig.3. Namely, Mn states are found at higher energies while Ni and Co states are found at lower energies as compared to iron states. Due to the model of the systems used in calculations, from the obtained electronic structure only a trend of band gap energies can be assumed. As seen at the Fig.3, partial substitution of iron by all studied transition metals is expected to influence decrease of band gap, and this decrease is expected to be the smallest in the case of Mn and largest in the case of Ni. In analogy to the results obtained in the study of Mg_2NiH_4[38], we find that Ni doping causes the largest disruption of Mg-H bond, and the largest change in both thermodynamical and optical properties.

The results of charge transfer analysis in the studied hydrides, based on the Bader's theory of atoms in molecules[45], are presented in Table 3. In all studied cases, the electrons are dominantly transferred from Mg to H in accordance with the electronegativity of atoms, and this agrees with the earlier studies of magnesium complex hydrides[32]. Small negative Bader charge is observed on all transition metals; and that is the main feature of charge transfer that distinguishes here studied complex hydrides from interstitial metallic hydrides[29,33]. Conclusion can be drawn that, although transition metal doping of Mg_2FeH_6 causes some changes in charge transfer, Bader charge of hydrogen atom is mainly unaffected and determined by type of interstitial site.

4. Conclusions

The influence of transition metal (Ni, Co, Mn) doping on the structural, electronic and hydrogen sorption properties of Mg_2FeH_6 is studied for the first time using first-principles density functional theory calculations. The thermodynamics of three different synthesis roots, proposed for Mg_2FeH_6, is addressed by calculating total energy changes in the formation reactions. We find that the calculated values show good agreement with experimental results where available. The smallest energy change is related to the reactions of MgH_2 transformation into complex hydrides, while the most excessive energy is related to the process of direct synthesis of complex hydrides. Doping with transition metals is found to destabilize all studied quaternary complex hydrides, $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Co,Ni) as compared to the staring Mg_2FeH_6. Regarding direct decomposition of studied hydrides, the largest decrease of desorption enthalpy is expected in the case of nickel doping, resulting in 27.7 $kJmol^{-1}H$ energy change instead of 39.4 $kJmol^{-1}H$ calculated for Mg_2FeH_6. Calculated contribution of zero point energy change to the total energy change is found to be the same for all hydrides in the same synthesis reaction. Obtained results are expected to be a good guidance in determination of reaction mechanisms for synthesis and decomposition of Mg_2FeH_6-based quaternary hydrides.

In addition, a detailed study of electronic structure reveals the influence of doping. The calculated width of the direct band gap of Mg_2FeH_6 is 1.85eV, while doping with Ni, Mn and Co leads to reduction of the direct band gap of Mg_2FeH_6. Some changes in charge transfer are identified based on calculation of the Bader charge, but the charge on hydrogen atom is mainly unaffected by doping and determined by type of interstitial site. According to the obtained results, Ni doping causes the largest disruption in the Mg_2FeH_6 lattice, and the largest change in both thermodynamical and optical properties.

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Acknowledgment:

The Ministry of Science and Technological Development of the Republic of Serbia provided the financial support for this study through the Project No.171 001.

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Table 1. Optimized lattice constants and Mg-H distances (obtained by GGA calculation) of the studied systems;

	a(Å)	$d_{Mg\text{-}H}$(Å)
Mg_2FeH_6	6.418 *6.443*[a]	2.269
$Mg_2Fe_{3/4}Mn_{1/4}H_6$	6.443	2.274
$Mg_2Fe_{3/4}Co_{1/4}H_6$	6.421	2.271
$Mg_2Fe_{3/4}Ni_{1/4}H_6$	6.442	2.276

[a] Ref.7

Table 2. Calculated change of electronic energy ΔE_{el} and zero point energy ΔE_{zpe} in the hydride formation reactions following three different mechanisms for Mg_2FeH_6 and $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Co,Ni)

	$Mg_2Fe_{3/4}Mn_{1/4}H_6$	Mg_2FeH_6	$Mg_2Fe_{3/4}Co_{1/4}H_6$	$Mg_2Fe_{3/4}Ni_{1/4}H_6$
Reaction 1	$2MgH_2+Fe(+H_2)\rightarrow Mg_2FeH_6$			
ΔE_{el} (kJ/molH)	-22.0	-27.8	-23.2	-16.3
ΔE_{zpe}(kJ/molH)	+4.5	+4.5	+4.5	+4.5
Reaction 2	$3MgH_2+Fe\rightarrow Mg_2FeH_6+Mg$			
ΔE_{el} (kJ/molH)	-13.5	-18.3	-14.7	-7.0
ΔE_{zpe}(kJ/molH)	+3.1	+3.1	+3.1	+3.1
Reaction 3	$2Mg+Fe+3H_2\rightarrow Mg_2FeH_6$			
ΔE_{el} (kJ/molH)	-39.1	-46.7	-40.4	-35.0
ΔE_{zpe}(kJ/molH)	+7.3	+7.3	+7.3	+7.3

Table 3. Charge transfer based on Bader AIM theory, for Mg_2FeH_6 and $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Co,Ni); the Bader charge equals the difference between the electronic charge of neutral atom and the electronic charge in the atomic basin of given atoms in the studied hydrides

	AIM charge/e			
	Mg	Fe	TM	H
Mg_2FeH_6	+1.66	-0.06	/	-0.55
$Mg_2Fe_{3/4}Ni_{1/4}H_6$	+1.66	-0.08	-0.01	-0.54
$Mg_2Fe_{3/4}Co_{1/4}H_6$	+1.66	-0.09	-0.02	-0.54
$Mg_2Fe_{3/4}Mn_{1/4}H_6$	+1.66	-0.02	-0.18	-0.56

Figure captions:

Fig.1 The unit cell of a) Mg_2FeH_6; b) $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Ni,Co);

Fig.2 Calculated total energy change during hydrogen desorption relevant to proposed mechanisms for $Mg_2Fe_{3/4}M_{1/4}H_6$ (M=Mn,Fe, Co, Ni) denoted by metal dopant at x-axes; reaction 1: $Mg_2FeH_6 \rightarrow 2MgH_2 + Fe + H_2$; reaction 2: $Mg_2FeH_6 + Mg \rightarrow 3MgH_2 + Fe$; reaction 3: $Mg_2FeH_6 \rightarrow 2Mg + Fe + 3H_2$; based on the calculated energy changes, direct decomposition (reaction 3) can easily be distinguished from other desorption mechanisms; experimental values of enthalpy for Mg_2FeH_6 taken from Ref.7 and Ref.8;

Fig.3 Total density of states in Mg_2FeH_6, $Mg_2Fe_{3/4}Mn_{1/4}H_6$, $Mg_2Fe_{3/4}Co_{1/4}H_6$ and $Mg_2Fe_{3/4}Ni_{1/4}H_6$ and partial contribution of Fe, Mn,Co and Ni states in these hydrides