

**Ab initio study of the effects of transition metal doping of Mg<sub>2</sub>NiH<sub>4</sub>**

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Mg<sub>2</sub>NiH<sub>4</sub> is a promising hydrogen storage material with fast (de)hydrogenation kinetics. Its hydrogen desorption enthalpy, however, is too large for practical applications. In this paper we study the effects of transition metal doping by first-principles density functional theory calculations. We show that the hydrogen desorption enthalpy can be reduced by  $\sim 0.1$  eV/H<sub>2</sub> if one in eight Ni atoms is replaced by Cu or Fe. Replacing Ni by Co atoms, however, increases the hydrogen desorption enthalpy. We study the thermodynamic stability of the dopants in the hydrogenated and dehydrogenated phases. Doping with Co or Cu leads to marginally stable compounds, whereas doping with Fe leads to an unstable compound. The optical response of Mg<sub>2</sub>NiH<sub>4</sub> is also substantially affected by doping. The direct gap in Mg<sub>2</sub>NiH<sub>4</sub> is  $\sim 1.7$  eV. Doping with Co, Fe, or Cu leads to impurity bands that reduce the direct gap by up to 0.5 eV.

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**I. INTRODUCTION**

The large scale application of hydrogen as a fuel depends on the development of materials that can store hydrogen in a dense form.<sup>1</sup> Magnesium based hydrides are interesting candidate materials for hydrogen storage, because magnesium has a low weight. The simplest hydride, MgH<sub>2</sub>, has a hydrogen storage capacity of 7.67 wt %. It has, however, a high hydrogen desorption enthalpy, 0.77 eV per H<sub>2</sub>, and hence an equilibrium plateau pressure ( $10^{-7}$  bar) at room temperature that is too low for practical applications.<sup>2</sup> Moreover, the hydrogen desorption and absorption reactions of MgH<sub>2</sub>/Mg suffer from kinetic barriers, which require operating temperatures in excess of 570 K. Various magnesium alloys have been studied to improve the thermodynamics and kinetics of the hydrogen desorption and absorption reaction.<sup>3-8</sup> Mg<sub>2</sub>NiH<sub>4</sub>, which can store 3.6 wt % of hydrogen, has been suggested as a candidate material, primarily because of its reasonably fast hydrogen desorption and absorption kinetics.<sup>9-15</sup> Several theoretical studies have been dedicated to Mg<sub>2</sub>NiH<sub>4</sub>.<sup>16-20</sup> However, its measured hydrogen desorption enthalpy of 0.70 eV per H<sub>2</sub> (Ref. 14) is barely lower than that of MgH<sub>2</sub>. It leads to an equilibrium hydrogen pressure of 1 bar at 510 K.<sup>15</sup> This temperature is far too high for applications using polymer electrolyte membrane (PEM) fuel cells, for instance. Apart from its possible role in hydrogen storage, Mg<sub>2</sub>Ni is also interesting because it can act as a switchable mirror.<sup>21-24</sup> Mg<sub>2</sub>Ni is a metal, whereas Mg<sub>2</sub>NiH<sub>4</sub> is a semiconductor with a band gap of 1.7–2.0 eV.<sup>25-27</sup> This leads to a remarkable change in the optical properties of the material upon hydrogenation and dehydrogenation. Especially if Mg<sub>2</sub>Ni is applied in thin films, the optical switching can be fast, reversible, and robust.<sup>28</sup> The high optical contrast opens up possibilities for Mg<sub>2</sub>Ni as a hydrogen sensing material.<sup>29-31</sup>

For both applications the reaction enthalpy of the hydrogen desorption and absorption at typical operating conditions

is too high. Preferable would be an equilibrium hydrogen pressure of 1 bar at room temperature. To reach this condition a hydrogen desorption enthalpy of 0.40 eV per H<sub>2</sub> is required. A substantial amount of experimental work has been dedicated to study the effects of doping of Mg<sub>2</sub>NiH<sub>4</sub> in order to reduce its hydrogen desorption enthalpy.<sup>28,32-41</sup> In this context “doping” means substituting a fairly large amount of Ni (or Mg) by other metals.

In this paper we report a study on the effects of doping Mg<sub>2</sub>NiH<sub>4</sub> with transition metals by first principles density functional theory (DFT) calculations. We restrict ourselves to the low-temperature (LT) phase of Mg<sub>2</sub>NiH<sub>4</sub>, since the high-temperature (HT) phase is stable only at elevated temperatures (i.e.,  $T > 500$  K) and therefore less relevant for applications.<sup>14</sup> We consider substitution of nickel by cobalt, iron, or copper in a concentration of 12.5%, which means substituting one in eight nickel atoms. This concentration is close to that used in recent experiments.<sup>42</sup> Our first aim is to monitor the change in hydrogen desorption enthalpy and, in particular, to establish which dopants (if any) lead to a reduction of the enthalpy. We show that zero point energies (ZPEs) associated with the hydrogen phonon modes considerably influence the enthalpies. Our second objective is to study the change in optical properties that results from doping. In particular we show that dopants in this concentration markedly alter the dielectric function.

**II. COMPUTATIONAL METHODS**

First principles DFT calculations are carried out using a plane wave basis set and the projector augmented wave (PAW) method,<sup>43,44</sup> as incorporated in the Vienna Ab initio Simulation Package (VASP).<sup>45-47</sup> We use the PW91 generalized gradient approximation (GGA) for the exchange correlation functional.<sup>48</sup> The cell parameters are kept at the experimental values and the atomic positions are relaxed using

a conjugate gradient algorithm. Nonlinear core corrections are applied.<sup>49</sup>

It has been shown for different classes of hydrides that to obtain accurate reaction enthalpies, ZPE contributions are important.<sup>50–52</sup> To calculate ZPEs we need the phonon frequencies of the materials involved. Phonon frequencies are calculated using a direct method,<sup>53</sup> i.e., the dynamical matrix is constructed from the force constants that are obtained from finite differences. Two opposite displacements of 0.05 Å are used for each atomic degree of freedom. In general one needs to carry out such calculations on a supercell containing several primitive unit cells, as the force constants do not go to zero within a distance corresponding to a single unit cell. However, the unit cells of the materials studied in this paper turn out to be sufficiently large, except for bulk magnesium, for which a  $2 \times 2 \times 2$  supercell is used. An advantage of large unit cells is that the phonon dispersion is small. It is therefore sufficient to calculate ZPEs from the phonon frequencies obtained at  $\Gamma$ .

The dielectric functions are calculated in the independent particle random phase approximation taking into account direct transitions from occupied to unoccupied Kohn-Sham orbitals only. We neglect excitonic, local field, and quasiparticle effects. The imaginary part of the macroscopic dielectric function then has the form

$$\begin{aligned} \varepsilon^{(2)}(\hat{\mathbf{q}}, \omega) = & \frac{8\pi^2 e^2}{V} \lim_{|\mathbf{q}| \rightarrow 0} \frac{1}{|\mathbf{q}|^2} \sum_{\mathbf{k}, v, c} | \langle u_{c, \mathbf{k}+\mathbf{q}} | u_{v, \mathbf{k}} \rangle |^2 \\ & \times \delta(\epsilon_{c, \mathbf{k}+\mathbf{q}} - \epsilon_{v, \mathbf{k}} - \hbar\omega), \end{aligned} \quad (1)$$

where  $\hat{\mathbf{q}}$  gives the direction of  $\mathbf{q}$ ;  $v$ ,  $\mathbf{k}$  and  $c$ ,  $\mathbf{k}$  label single particle states that are occupied, unoccupied in the ground state, respectively;  $\epsilon$ ,  $u$  are the single particle energies and the translationally invariant parts of the wave functions, respectively;  $V$  is the volume of the unit cell. Further details can be found in Ref. 54.

Almost all experimental optical data on hydrides are obtained from micro- or nanocrystalline samples whose crystallites have a significant spread in orientation. The most relevant quantity then is the directionally averaged dielectric function, i.e.,  $\varepsilon^{(2)}(\omega)$  averaged over  $\hat{\mathbf{q}}$ . In this paper we only report directionally averaged dielectric functions.

The Brillouin zone integrations are performed using a modified tetrahedron method.<sup>55</sup> All calculations on the hydrides use a  $7 \times 7 \times 7$  Monkhorst-Pack  $\mathbf{k}$ -point mesh for sampling the Brillouin zone, and the calculations on the metals use a  $7 \times 7 \times 3$  Monkhorst-Pack  $\mathbf{k}$ -point mesh.<sup>56</sup> We use 480 bands to calculate the dielectric function. This number of bands includes all transitions up to 30 eV. For the materials containing copper a plane wave kinetic energy cutoff of 341 eV is used, and for the other materials a cutoff of 337 eV. To obtain accurate formation and reaction enthalpies, the total energies of all final structures are calculated using a plane wave kinetic energy cutoff of 700 eV.

### III. STRUCTURE AND STABILITY OF UNDOPED MATERIALS: $\text{Mg}_2\text{NiH}_4$ , $\text{Mg}_2\text{CoH}_5$ , $\text{Mg}_2\text{FeH}_6$ , $\text{Mg}_2\text{Ni}$ , AND ELEMENTAL METALS

In order to assess the stability of doped  $\text{Mg}_2\text{NiH}_4$  we first need the total energies of the undoped hydrides and of all

elemental metals involved. The optimized structures of  $\text{Mg}_2\text{NiH}_4$ ,  $\text{Mg}_2\text{CoH}_5$ , and  $\text{Mg}_2\text{FeH}_6$  are given in Table I. They are in good agreement with the experimental structures.<sup>57–59</sup> The metal atoms in LT  $\text{Mg}_2\text{NiH}_4$  form a distorted  $\text{CaF}_2$ -type structure. Four hydrogen atoms are arranged around each nickel atom in a tetrahedron. In  $\text{Mg}_2\text{FeH}_6$  and  $\text{Mg}_2\text{CoH}_5$  the Mg and Fe/Co atoms form an undistorted  $\text{CaF}_2$ -type structure. In  $\text{Mg}_2\text{FeH}_6$  the hydrogen atoms form regular octahedra around the iron atoms. In  $\text{Mg}_2\text{CoH}_5$  the hydrogen atoms occupy five corners of a slightly distorted octahedron around each cobalt atom.

The experimental structure of  $\text{Mg}_2\text{Ni}$  can be found in Ref. 12. The unit cell contains 12 Mg and 6 Ni atoms, which are basically hexagonally close-packed. The optimized structure given in Table I is in good agreement with experiment. For  $\text{MgH}_2$  we use a previously calculated structure.<sup>50</sup> For the elemental metals and  $\text{MgCu}_2$  we use the experimental lattice parameters, i.e.,  $a(c) = 3.21(5.21)$  Å,  $a = 2.87$  Å,  $a(c) = 2.51(4.07)$  Å,  $a = 3.52$  Å,  $a = 3.61$  Å, and  $a = 7.03$  Å for Mg, Fe, Co, Ni, Cu, and  $\text{MgCu}_2$ , respectively.<sup>60</sup> The magnetic elements iron, cobalt, and nickel are treated by spin-polarized calculations. The calculated pressures are small, indicating that it is unnecessary to explicitly optimize the lattice parameters. We explicitly tested the latter for iron, since there the external pressure was largest, and obtained an energy gain of less than 0.01 eV.

In order to obtain accurate enthalpies for reactions involving materials that contain hydrogen, one has to take ZPEs into account. All calculated total energies and ZPEs are given in Table II. We neglect the ZPEs of the elemental metals. The ZPE for magnesium is only 0.03 eV/atom. The ZPEs of iron, cobalt, nickel, and copper will be even smaller, since the atomic weight of those elements is more than twice that of Mg.

ZPE corrections are significant in reactions where hydrogen molecules are adsorbed or desorbed. They arise mainly from the difference between the number and frequencies of the vibrational modes of the hydrogen atoms in a solid host and those of the hydrogen molecules. If the bonding of hydrogen atoms does not change much in a reaction, the ZPE correction is small. One can expect this to be the case for the possible phase segregation reaction of doped  $\text{Mg}_2\text{NiH}_4$ , see Eq. (5), where we neglect the ZPE correction. We checked this assumption explicitly for Fe-doped  $\text{Mg}_2\text{NiH}_4$  and found the ZPE correction to be 1 meV/ $\text{H}_2$ .

To calculate hydrogen desorption enthalpies we also need the total energy of the hydrogen molecule. It is calculated using a cubic cell with sides of 13 Å. We find an equilibrium distance of 0.7486 Å, a vibrational frequency of 4350  $\text{cm}^{-1}$ , and a dissociation energy of 4.57 eV, which compare reasonably well with the experimental values of 0.7461 Å, 4401  $\text{cm}^{-1}$ , and 4.48 eV, respectively.<sup>60,61</sup> The 0.1 eV deviation in the dissociation energy of  $\text{H}_2$  is relatively large in view of the accuracy required for calculating hydrogen desorption enthalpies. This 0.1 eV may be considered as a correction to the reaction enthalpies discussed below.

We calculate the ZPE for the hydrogen molecule from the energy levels of a Morse potential,

TABLE I. Calculated atomic positions of Mg<sub>2</sub>NiH<sub>4</sub> (experiment, Ref. 57), Mg<sub>2</sub>CoH<sub>5</sub> (experiment, Ref. 58), Mg<sub>2</sub>FeH<sub>6</sub> (experiment, Ref. 59), and Mg<sub>2</sub>Ni (experiment, Ref. 12). In the calculations the lattice parameters were kept at the experimental values.

Compound	Space group unit cell			x	y	z
Mg <sub>2</sub> NiH <sub>4</sub>	<i>C2/c</i> (15) $\beta=113.52^\circ$ $a=14.343 \text{ \AA}$ $b=6.4038 \text{ \AA}$ $c=6.4830 \text{ \AA}$	Mg	8 <i>f</i>	0.2646	0.4863	0.0833
		Mg	4 <i>e</i>	0	0.0252	0.2500
		Mg	4 <i>e</i>	0	0.5264	0.2500
		Ni	8 <i>f</i>	0.1199	0.2294	0.0801
		H	8 <i>f</i>	0.2088	0.3048	0.3041
		H	8 <i>f</i>	0.1390	0.3192	0.8760
		H	8 <i>f</i>	0.0096	0.2908	0.0527
		H	8 <i>f</i>	0.1243	0.9866	0.0727
Mg <sub>2</sub> CoH <sub>5</sub>	<i>P4/nmm</i> (129) $a=4.463 \text{ \AA}$ $c=6.593 \text{ \AA}$	Mg	2 <i>a</i>	3/4	1/4	0
		Mg	2 <i>b</i>	3/4	1/4	1/2
		Co	2 <i>c</i>	1/4	1/4	0.2567
		H	2 <i>c</i>	1/4	1/4	0.4947
		H	8 <i>j</i>	0.4914	0.4914	0.2268
Mg <sub>2</sub> FeH <sub>6</sub>	<i>Fm3m</i> (225) $a=6.437 \text{ \AA}$	Mg	8 <i>c</i>	1/4	1/4	1/4
		Fe	4 <i>a</i>	0	0	0
		H	24 <i>e</i>	0.2425	0	0
Mg <sub>2</sub> Ni	<i>P6<sub>3</sub>22</i> (180) $\gamma=120^\circ$ $a=5.205 \text{ \AA}$ $c=13.236 \text{ \AA}$	Mg	6 <i>i</i>	0.1639	0.3278	0
		Mg	6 <i>f</i>	1/2	0	0.1165
		Ni	3 <i>b</i>	0	0	1/2
		Ni	3 <i>d</i>	1/2	0	1/2

$$E(n) = \hbar\omega \left( n + \frac{1}{2} \right) - \frac{1}{4D_e} \left[ \hbar\omega \left( n + \frac{1}{2} \right) \right]^2, \quad (2)$$

where  $\omega$  is the vibration frequency and  $D_e$  is the dissociation energy. The result is given in Table II.

#### IV. DOPED Mg<sub>2</sub>NiH<sub>4</sub> and Mg<sub>2</sub>Ni

##### A. Structure

The unit cell of the LT phase of Mg<sub>2</sub>NiH<sub>4</sub> contains eight formula units. To simulate doping we replace one of the Ni atoms by a Fe, Co, or Cu atom, thus achieving a 7:1 ratio

between Ni and dopant atoms. In simple terms one can think of undoped Mg<sub>2</sub>NiH<sub>4</sub> as being constructed from Mg<sup>2+</sup> and (NiH<sub>4</sub>)<sup>4-</sup> ions. The latter involve 18 valence electrons and are closed shell ions. Upon doping it is likely that in the fully hydrogenated phase the closed shell character is maintained. This means that (NiH<sub>4</sub>)<sup>4-</sup> is replaced by (FeH<sub>6</sub>)<sup>4-</sup>, (CoH<sub>5</sub>)<sup>4-</sup>, or (CuH<sub>3</sub>)<sup>4-</sup>. Thus for an Fe atom we add two extra hydrogen atoms, one for a Co atom, and for a Cu atom we remove one hydrogen atom. For all doped systems we fix the unit cell to that of undoped Mg<sub>2</sub>NiH<sub>4</sub> and we optimize the atomic positions. The external pressures on the doped systems are small, which indicates that the gain in energy when relaxing the cell volumes will not be significant. From Vegard's law one can

TABLE II. Calculated total energies and ZPEs of the undoped hydrides and metals per formula unit.

	<i>E</i> (eV)	ZPE (eV)		<i>E</i> (eV)	ZPE (eV)
H <sub>2</sub>	-6.803	0.266	MgH <sub>2</sub>	-8.983	
Mg	-1.524	0.030	Mg <sub>2</sub> Ni	-9.133	0.102
Fe	-8.150		Mg <sub>2</sub> FeH <sub>6</sub>	-34.511	
Co	-6.841		Mg <sub>2</sub> CoH <sub>5</sub>	-29.355	
Ni	-5.459		Mg <sub>2</sub> NiH <sub>4</sub>	-24.053	0.852
Cu	-3.725		MgCu <sub>2</sub>	-9.45	

estimate the volume relaxation caused by the Fe and Co dopants, using the volumes of  $\text{Mg}_2\text{NiH}_4$ ,  $\text{Mg}_2\text{CoH}_5$ , and  $\text{Mg}_2\text{FeH}_6$ . The expected volume relaxation is less than 0.5%. Its effect on the hydrogen desorption enthalpy is less than 1 meV/ $\text{H}_2$ .

The geometry of the hydrogens around the Fe and Co dopant atoms resembles the geometry in  $\text{Mg}_2\text{FeH}_6$  and  $\text{Mg}_2\text{CoH}_5$ , respectively. In  $\text{Mg}_2\text{FeH}_6$  each Fe atom is in the center of a perfect octahedron of hydrogen atoms with an Fe-H distance of 1.56 Å. In Fe doped  $\text{Mg}_2\text{NiH}_4$  the octahedron is distorted. The H-Fe-H angles range from 80° to 100° and the Fe-H distances range from 1.55 to 1.58 Å in the case where a H atom is only bonded to an Fe atom. However, four of the hydrogen atoms surrounding an Fe atom also bond to Ni atoms, in which case the Fe-H distance is enlarged to 1.64–1.76 Å. The hydrogen tetrahedra around such Ni atoms are distorted with Ni-H distances ranging from 1.51 to 1.80 Å, whereas in undoped  $\text{Mg}_2\text{NiH}_4$  they are between 1.56 and 1.58 Å.

In the case of Co doping the distortions are much smaller. In  $\text{Mg}_2\text{CoH}_5$  the hydrogen atoms surrounding each Co atom form a four-sided pyramid with the Co atom just above the basal plane of the pyramid. To describe the geometry we denote the basal plane hydrogens by  $H_b$  and the top hydrogen by  $H_t$ . The  $H_b$ -Co- $H_b$  angle is 89°, the Co- $H_b$  distance is 1.52 Å, the  $H_b$ -Co- $H_t$  angle is 97.6° and the Co- $H_t$  distance is 1.59 Å. The Co-Mg distances range from 2.75 to 2.80 Å. The hydrogens surrounding the Co atom in doped  $\text{Mg}_2\text{NiH}_4$  form a slightly distorted pyramid, with  $H_b$ -Co- $H_b$  angles ranging from 83.1° to 94.1° and Co- $H_b$  distances ranging from 1.53 to 1.56 Å. The  $H_b$ -Co- $H_t$  angle is 93.4° to 105.1° and the Co- $H_t$  distance is 1.57 Å. The Co-Mg distances vary from 2.69 to 2.80 Å. The Ni-H bond lengths are not affected by Co doping.

We cannot compare the geometry of the hydrogens in Cu doped  $\text{Mg}_2\text{NiH}_4$  to  $\text{Mg}_2\text{CuH}_3$ , since the latter compound is not stable with respect to decomposition into  $\text{MgH}_2$  and  $\text{MgCu}_2$ .<sup>32</sup> The Ni-H distances in Cu doped  $\text{Mg}_2\text{NiH}_4$  are similar to those in undoped  $\text{Mg}_2\text{NiH}_4$ . The hydrogen atoms surrounding the Cu atom are located at three corners of a tetrahedron with the Cu atom in the center. The Cu-H distances, 1.62–1.64 Å, are slightly larger than the Ni-H distances, 1.56–1.59 Å.

### B. Reaction enthalpies

In order to calculate the hydrogen desorption enthalpy of doped  $\text{Mg}_2\text{NiH}_4$  we also need the total energy of doped  $\text{Mg}_2\text{Ni}$ . The unit cell of  $\text{Mg}_2\text{Ni}$  contains six formula units per cell. If we replace one of the Ni atoms in this cell by a dopant atom, this gives a 5:1 Ni:dopant ratio, instead of the required 7:1 ratio. We approximate the total energy of the 7:1 ratio by the average energy of three 5:1 doped unit cells and one undoped cell. All calculated total energies and ZPEs of the doped hydrides and metals are given in Table III.

From the data in Table III we calculate the desorption enthalpy per  $\text{H}_2$  molecule,

$$E_{\text{des}} = E(\text{H}_2) + \frac{2}{x} [E(\text{Mg}_2\text{Ni}_{7/8}\text{TM}_{1/8}) - E(\text{Mg}_2\text{Ni}_{7/8}\text{TM}_{1/8}\text{H}_x)], \quad (3)$$

where  $E(M)$  is the total energy of compound  $M$  and  $x$  is the

TABLE III. Calculated total energies, ZPEs, and hydrogen content of the doped hydrides,  $\text{Mg}_2\text{Ni}_{7/8}\text{TM}_{1/8}\text{H}_x$ , and the metals,  $\text{Mg}_2\text{Ni}_{7/8}\text{TM}_{1/8}$ . The values are per formula unit.

TM	$E$ (eV)	ZPE (eV)	$x$ (no. H)
Fe	-24.952	0.914	4.250
Co	-24.677	0.876	4.125
Ni	-24.053	0.852	4.000
Cu	-23.207	0.826	3.875
Fe	-9.278	0.100	
Co	-9.233	0.100	
Ni	-9.133	0.102	
Cu	-8.890	0.102	

number of hydrogen atoms in the hydride. The latter depends upon the dopant atom, as discussed in the previous section. The values of  $x$  are given in Table III.

The calculated desorption enthalpy of undoped  $\text{Mg}_2\text{NiH}_4$  is 0.66 eV/ $\text{H}_2$  without ZPE and 0.55 eV/ $\text{H}_2$  with ZPE. The corresponding experimental value is 0.70 eV/ $\text{H}_2$ .<sup>14</sup> We find that the ZPE corrected desorption enthalpies are consistently lower than the experimental values by 0.1–0.2 eV/ $\text{H}_2$ .<sup>50,62</sup> However, the relative error in similar compounds, such as the MgTM hydrides studied here, is less than  $\sim 0.05$  eV/ $\text{H}_2$ . One source of error could be the overestimation of the  $\text{H}_2$  dissociation energy by 0.1 eV, mentioned in Sec. III. If we assume that the desorption enthalpies can be corrected (i.e., increased) by this amount, it brings them within  $\sim 0.1$  eV/ $\text{H}_2$  of the experimental values. In the following we give the uncorrected results only. Note, however, that this correction opposes the ZPE correction. It has been observed before that calculated desorption enthalpies without ZPE corrections can be closer to experimental values.<sup>62,63</sup>

The results for  $E_{\text{des}}$  of doped  $\text{Mg}_2\text{NiH}_4$  are given in Fig. 1. These results clearly demonstrate that the desorption enthalpy can be tuned by an appropriate doping. The desorption enthalpy decreases considerably both for Fe and for Cu doping, i.e., by 84 and 71 meV per  $\text{H}_2$ , respectively. However, Co doping increases the desorption enthalpy by 28 meV per  $\text{H}_2$ . The trends for Cu and Fe doping are in qualitative agreement with experimental data.<sup>32,38,41</sup>

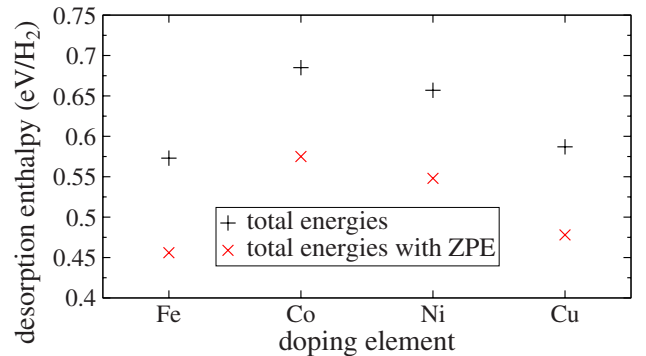


FIG. 1. (Color online) Desorption enthalpies  $E_{\text{des}}$  (eV/ $\text{H}_2$ ) of the doped hydrides.

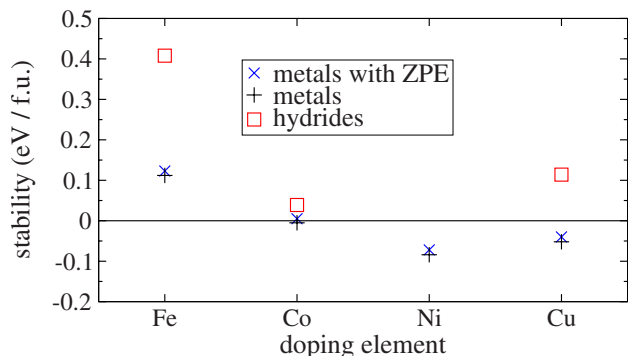
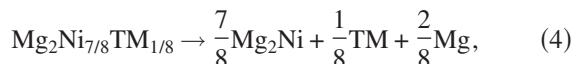


FIG. 2. (Color online) Stability with respect to phase segregation (eV/f.u.). Values are negative if the compound is stable, see Eqs. (4)–(6).

Figure 1 also shows the calculated desorption enthalpies corrected with ZPEs. The ZPEs of all the metals are almost identical, see Table III, and the ZPEs of the hydrides scale linearly with the amount of hydrogen atoms. This means that the ZPE per hydrogen atom is almost constant and independent of the dopant atom. Therefore the ZPE correction to the desorption enthalpy per  $H_2$  is 0.1 eV for all compounds studied.

### C. Stability

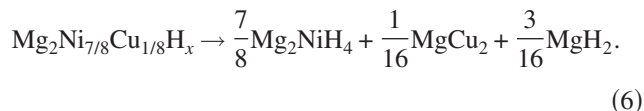
Doped  $Mg_2NiH_4$  is stable in thin films.<sup>42</sup> In order to assess whether kinetics plays an important role in stabilizing these compounds, we study the thermodynamic stability of the doped materials with respect to phase segregation. For the dehydrogenated doped  $Mg_2Ni$  metal we consider decomposition into  $Mg_2Ni$ , bulk magnesium, and bulk doping metal,



where  $TM=Fe, Co, \text{ or } Cu$ . Fully hydrogenated undoped  $Mg_2NiH_4$  is compared to bulk nickel and  $MgH_2$ . For the hydrogenated doped  $Mg_2NiH_4$  we consider decomposition into phase segregated  $Mg_2NiH_4$  and  $Mg_2FeH_6$  or  $Mg_2CoH_5$ ,



with  $x$  as in Table III and  $y=5,6$  for  $Co, Fe$ , respectively. Since  $Mg_2CuH_3$  is unstable with respect to decomposition into  $MgH_2$  and  $MgCu_2$ , we consider for the hydrogenated Cu doped  $Mg_2NiH_4$  the possible decomposition reaction



The results are shown in Fig. 2.

Fe doped  $Mg_2Ni$  is thermodynamically unstable with respect to phase segregation into  $Mg_2Ni$  bulk Mg and bulk Fe. Co doped  $Mg_2Ni$  is a marginally unstable material in which

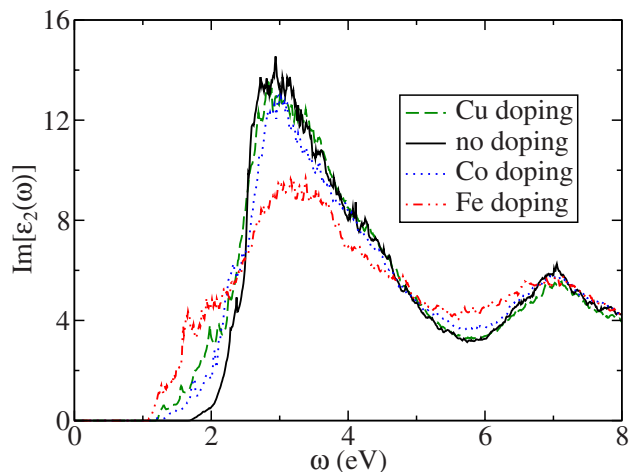


FIG. 3. (Color online) Imaginary part of the frequency dependent dielectric functions of doped  $Mg_2NiH_4$ .

segregation is favored by only  $\sim 0.01$  eV per formula unit. Fe, Co doped  $Mg_2NiH_4$  are thermodynamically unstable with respect to segregation into  $Mg_2NiH_4$  and  $Mg_2FeH_6$ ,  $Mg_2CoH_5$ , respectively. Doping of  $Mg_2Ni$  with Cu leads to a stable material. Experimental work proved the stability of  $Mg_2Ni_{1-x}Cu_x$  solid solutions;<sup>32,40</sup> for  $0 < x < 0.85$  these compounds are isostructural with  $Mg_2Ni$ . Experiment indicates that the hydrogenated phase decomposes into  $MgH_2$ ,  $MgCu_2$ , and  $Mg_2NiH_4$ .<sup>32</sup> This is confirmed by our calculations, see Fig. 2.

In conclusion, many of the doped phases are thermodynamically unstable. This does not need to hamper their usefulness, however, since kinetics plays an important role in stabilizing the doped compounds. The hydrogen desorption temperature lies far below the temperature that is used to anneal these materials.<sup>42</sup> The Cu doped  $Mg_2Ni$  metal is thermodynamically stable, and hydrogenating this material can lead to a useful metastable compound.

### V. OPTICAL PROPERTIES

The imaginary part of the dielectric function and the electronic density of states (DOS) of undoped  $Mg_2NiH_4$  are shown in Figs. 3 and 4, respectively. They are in good agreement with the results of previous calculations.<sup>19,20</sup> We find an indirect band gap of 1.6 eV and a direct gap of 1.7 eV. This is in good agreement with the experimental direct gap of 1.7–2.0 eV.<sup>25–27</sup> The agreement is in fact remarkable since DFT usually underestimates the band gap by 30–50%. For  $Mg_2FeH_6$  and  $Mg_2CoH_5$  we obtain direct gaps of 1.8 and 1.3 eV, respectively. The latter is in good agreement with the experimental gap of 1.5 eV.<sup>64</sup> Shifts in band gaps upon doping can therefore be calculated reliably. The agreement between the calculated DFT gaps and the experimental optical gaps for these MgTM hydrides might be somewhat fortuitous. However, it means that we can refrain from calculating the quasiparticle spectrum, which is often needed to obtain the correct band gaps in hydrides.<sup>65–67</sup>

The dielectric function of  $Mg_2NiH_4$  has two peaks, which can be directly related to the two peaks in the DOS of the

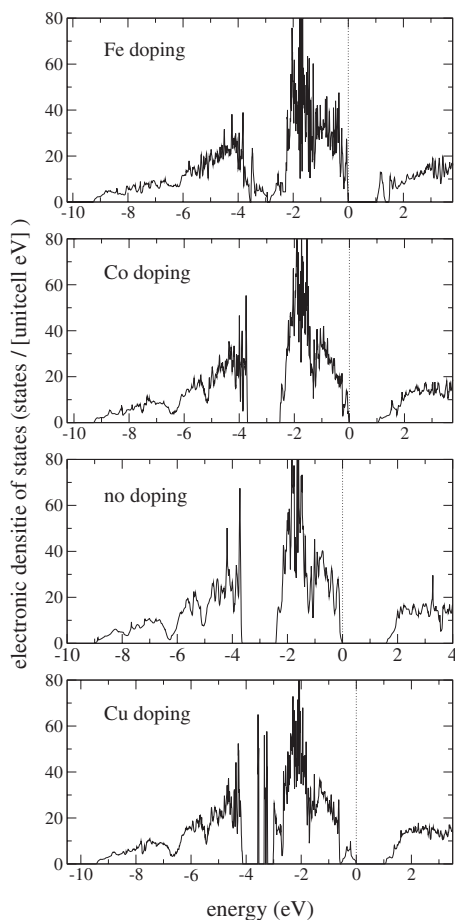


FIG. 4. Electronic densities of state of doped  $\text{Mg}_2\text{NiH}_4$ . The Fermi level is at the top of the valence bands. The four DOSs are aligned at the bottom of the valence band.

valence bands. The dielectric functions of doped  $\text{Mg}_2\text{NiH}_4$  are also shown in Fig. 3. Doping alters the dielectric function and, remarkably, the size of the change correlates with the change in hydrogen desorption enthalpy caused by the dopants, see Fig. 1. This can be explained by noticing that both changes have a common cause. The changes in desorption enthalpy are due to changes in metal-hydrogen bond lengths and bond energies. Changes in bond energies shift the energy levels and hence can be detected in the optical spectrum. Such changes are largest in Fe doped  $\text{Mg}_2\text{NiH}_4$ . An Fe dopant atom includes two extra hydrogen atoms. It gives the largest perturbation in the  $\text{Mg}_2\text{NiH}_4$  lattice, with almost half of the metal-hydrogen bond lengths being changed with respect to the undoped case.

The DOS of doped  $\text{Mg}_2\text{NiH}_4$  is given in Fig. 4. To facilitate an internal comparison the DOS of all compounds is aligned at the bottom of the valence band. Besides the fundamental gap between the valence and conduction bands, we can identify a clear gap in the valence bands, between 2.4 and 3.6 eV below the Fermi level in undoped  $\text{Mg}_2\text{NiH}_4$ . The states above this valence gap have a strong metal  $d$  character, whereas the lower valence states have a dominant hydrogen character. Cu and Fe doping introduces states in the valence gap, whereas all dopants introduce states in the fundamental

gap. In the case of Cu doping these appear near the top of the valence band, whereas for Co and Fe doping gap states appear near the bottom of the conduction band. Since we have adjusted the amount of hydrogen upon doping, all doped materials are semiconducting.

The DOS can be used to interpret the dielectric functions. The decrease in the fundamental gap in the DOS upon doping gives a decrease in the direct gaps. The largest changes in the dielectric function are observed upon Fe doping. The highest peak decreases as compared to the undoped case and the valley between the two peaks is less deep. In addition, a distinct shoulder appears at low energy. Fe doping gives a clear peak in the DOS at the bottom of the conduction band, which yields the distinct shoulder in the dielectric function. The two main peaks in the dielectric functions are not shifted upon doping. This indicates that the dopants mainly give rise to additional features via the introduction of gap states, as can be observed in the DOS. Similar conclusions hold for the Cu and Co doped cases, but the perturbation of the  $\text{Mg}_2\text{NiH}_4$  DOS caused by doping is smaller than for the Fe doped case.

## VI. CONCLUSIONS

$\text{Mg}_2\text{NiH}_4$  is a promising hydrogen storage material with fast (de)hydrogenation kinetics. Its hydrogen desorption enthalpy, however, is too large for practical applications. In this paper we study the effects of transition metal doping by first-principles density functional theory calculations. We show that the hydrogen desorption enthalpy can be reduced by 0.1 eV/ $\text{H}_2$  if one in eight Ni atoms is replaced by Cu or Fe. Replacing Ni by Co atoms, however, increases the hydrogen desorption enthalpy. We study the thermodynamic stability of the dopants in the hydrogenated and dehydrogenated phases. All hydrides turn out to be unstable with respect to phase segregation. Doping with Co or Cu leads to marginally stable metals, whereas doping with Fe leads to an unstable metal. The optical response of  $\text{Mg}_2\text{NiH}_4$  is also substantially affected by doping. The direct gap in  $\text{Mg}_2\text{NiH}_4$  is  $\sim 1.7$  eV. Doping with Co, Fe, or Cu leads to impurity bands that reduce the direct gap by up to 0.5 eV.

We study the effects of transition metal doping on the hydrogen desorption enthalpy and the optical properties of  $\text{Mg}_2\text{NiH}_4$  by first-principles DFT calculations. The desorption enthalpy is reduced by 84 meV per  $\text{H}_2$ , if one in eight Ni atoms is replaced by an Fe atom. Replacing one in eight Ni atoms by a Cu atom reduces the desorption enthalpy by 71 meV/ $\text{H}_2$ , but replacement by a Co atom increases it by 28 meV/ $\text{H}_2$ . Including energy corrections due to the zero point motions of the atoms changes the absolute values of the desorption energies by 0.1 eV/ $\text{H}_2$ . Since, however, the zero point energies per hydrogen atom are almost independent of the compound studied, the relative values of the desorption energies are not affected.

The thermodynamic stabilities of the doped dehydrogenated  $\text{Mg}_2\text{Ni}$  and the fully hydrogenated  $\text{Mg}_2\text{NiH}_4$  compounds are studied by considering possible decomposition reactions. The results show that Cu doped  $\text{Mg}_2\text{Ni}$  is stable, Co doped  $\text{Mg}_2\text{Ni}$  is marginally stable, and Fe doped  $\text{Mg}_2\text{Ni}$  is unstable with respect to phase separation into  $\text{Mg}_2\text{Ni}$ , bulk

Mg and the bulk transition metal dopant. The doped hydrogenated  $\text{Mg}_2\text{NiH}_4$  compounds are either marginally unstable in the case of Co or Cu doping, or, in the case of Fe doping, clearly unstable. Kinetic barriers could be sufficiently high to stabilize metastable doped compounds since the hydrogen desorption temperatures are smaller than the temperatures used to anneal these materials. Nevertheless, thermodynamics indicates that Cu is the most promising candidate to lower the hydrogen desorption enthalpy of  $\text{Mg}_2\text{NiH}_4$ .

By calculating the dielectric function within the random phase approximation we study the effects of doping on the optical properties of  $\text{Mg}_2\text{NiH}_4$ . The changes in the dielectric function can be interpreted in terms of the electronic densities of states of the corresponding compounds. The dopant atoms introduce states in the fundamental gap, as well as below the valence Ni  $d$  band. These states cause a shift in the onset of absorption to lower energy by up to 0.5 eV and they decrease the relative heights of the peaks in the  $\text{Mg}_2\text{NiH}_4$

absorption spectrum. The sizes of these changes correlate with the change in the hydrogen desorption enthalpy caused by the dopants. Fe doping causes the largest disruption in the  $\text{Mg}_2\text{NiH}_4$  lattice, and the largest change in the optical properties.

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