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Hydrogen occupancy in the RNi$_4$Mg (R=Y, La, Ce, and Nd) intermetallic compounds and hydrides

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We have investigated the effect of hydrogen on the electronic strtucture of the RNi$_4$Mg (R=Y, La, Ce, Pr, and Nd) intermetallics. By means of a two-step approach, the projected plane-wave and linearized plane-waves methods, we studied the hydrogen-insertion energetics on the intermetallic matrix and the H-vacancy formation in the hydride compound. We found that particular interstitial sites in the intermetallics are suitable to allocate hydrogen and form a solid solution. The effect of these interstitials on the electronic structure is discussed. In the other hand, the hydrogen-occupied sites in the hydride are found to be energetically equivalent.

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I. INTRODUCTION

Hydrogen in intermetallic compounds has retained an enormous interest in the last decades owing to their use in hydrogen storage and batteries as well as other potential applications. The RNi$_4$Mg (R=Y, La, Ce, Pr, and Nd) intermetallic series belong to the SnMgCu$_4$ (AuBe$_4$-type) structure. This kind of solids exhibits a $F\bar{4}3m$ space group, closely related to the Laves C15 structure. This family of intermetallic compounds interacts with hydrogen and forms highly stoichiometric hydrides having moderate equilibrium hydrogen partial pressures at room temperature making them suitable for hydrogen storage. Besides this potential ability to match application requirements, the hydrogen behavior in the low as well as high H content regime is of a fundamental interest since these compounds exhibit (1) anisotropic lattice modifications and (2) a phase transformation as the H content increases. The hydriding properties of these compounds have been shown by Aono *et al.*[1] in the YNi$_4$Mg system. Kadir *et al.*[2] investigated systematically the structural properties of ANi$_4$Mg (A=Ca, La, Ce, Pr, Nd, and Y). They concluded that all the listed compounds crystallize in the above mentioned structure exhibiting intermetallic distances consistent with a metallic bonding. Hanada *et al.*[3] call the attention to the hydriding properties of the Ca and Y compounds. They state that while the YNi$_4$Mg does not exhibit substitutional disorder, the CaNi$_4$Mg does. The substitutional disorder seems to improve the maximum-hydrogen stoichiometry of the resulting hydrides. Guénée *et al.*[4] have successfully synthesized the NdNi$_4$Mg intermetallic compound and the corresponding hydride. They rise up the question of possible phase segregation during the alloy preparation, in particular, for LaNi$_4$Mg. However, they precisely determine the site occupancy for hydrogen in the NdNi$_4$MgH$_{3.6}$ which belongs to the orthorhombic $Pmn2_1$ space group. Wang *et al.*[5] claim a single-phase preparation of the full series RNi$_4$Mg (R=La, Ce, Pr, Nd, and Y) by considering an excess of 5% of Mg over the stoichiometric starting metal blend. This is explained by the high volatility (low meting point) of Mg respect to the other metals in the formula. However, the possibility of segregation still remains open to investigation. In a recent research, Roquefere *et al.*[6,7] found that the CeNi$_4$Mg intermetallic decomposes under hydrogenation producing the more stable CeH$_{2.5}$ hydride.

We investigated the electronic properties of these compounds in order to provide a better understanding of the H-host interaction. In addition, we compute the energy associated to hydrogen insertion in the hydrogen-free intermetallic as well as the hydrogen withdraw from the hydride. In the following section we summarize the methodological choices then we describe our findings in the different H-content regions and finally we summarize our results and conclusions.

II. METHODOLOGY

The electronic structure of the four intermetallic compounds under investigation has been computed using a two-step approach. First, a full geometry optimization using a pseudopotential scheme and then carrying out an all-electron linear-augmented plane-waves (LAPW) computation of the energy bands and density of states. This is a successful approach that has been already employed in our most recent work in this area.[8–10] Geometry optimizations of the crystal structures were obtained by means of the projected-augmented plane-wave method (PAW).[11] We employed PAW pseudopoptentials and the generalized gradient approximation (GGA) to the exchange and correlation potential.[12] In the case of Ce and Nd compounds, we introduced a GGA $+U$ correction[13–15] for the rare-earth $4f$ electrons fixing $U_{eff}=U\text{-}J=5$ eV. All the crystal structures were converged to local forces below 10^{-2} eV/Å. Energy bands have been computed on a set of special k-points within the Brillouin zone. The sampling has been done by the Monkhorst-Pack[16] technique selecting up to a $3\times3\times2$ grid for the intermetallics and hydrides and $1\times1\times1$ grid for the large supercells (Γ-point computation). To compute the H-energy site, we construct supercells and insert/remove an H atom from the structure of the intermetallic/hydride. Details of these computations will be described in the following section. *Ab initio* calculations of the electronic structure of the intermetallic

TABLE I. Structural details of $R\mathrm{Ni}_4\mathrm{Mg}$ (R=Y, La, Ce, and Nd) intermetallics. Lattice parameters (in Å); Experimental a_{exp} taken from Wang *et al.* (Ref. 5) computed a_{PAW}, Δa, and relative error.

	a_{exp}	a_{PAW}	Δa (%)
Y	7.0104	7.0077	−0.04
La	7.1559	7.1428	−0.18
Ce	7.0040	7.0344	0.43
Nd	7.0836	7.1428	−0.04

compounds $R_2\mathrm{MgNi}_4$ and the corresponding hydrides $R\mathrm{Ni}_4\mathrm{MgH}_4$ (R=Y, La, Ce, and Nd) were carried out by means of the all-electron full potential LAPW method.[17] The muffin-tin radii were set to 2.20, 1.80, 2.0, and 1.0 a.u. for the R, Ni, Mg, and H atoms, respectively. The RK_{max} parameter, which controls the plane-wave expansion, was selected in order to obtain converged eigenvalues up to 10^{-3} eV, ($RK_{max}=7$). The sampling of the irreducible wedge of Brillouin zone included up to 120 k points for intermetallics and hydrides and this has been reduced to around 40 k points for large supercells. We employed the GGA to the exchange and correlation density functional.[12] Self-interaction corrections were introduced in the compounds containing Ce and Nd. As in the PAW computations U_{eff} was set to 5 eV. Total density of states (DOS) and partial density of states (PDOS) were computed by tetrahedra integration of the energy bands obtained with the LAPW method.

III. RESULTS AND DISCUSSION

A. Intermetallic compounds

The intermetallic compounds $R\mathrm{Ni}_4\mathrm{Mg}$ (R=Y, La, Ce, and Nd) belongs to the face-centered-cubic $F\bar{4}3m$ space group of the $\mathrm{MgCu}_4\mathrm{Sn}$-type structure. Aside the well-determined structure it is important to mention that these compounds exhibit different degrees of substitutional disorder as it has been indicated in the Introduction. Nevertheless, we have approximated the real structure of these compounds to the fully ordered crystals. We come back to this substitutional disorder below. The PAW-computed lattice parameters as well as the symmetry unconstrained coordinates of the atoms in the unit cell exhibit an excellent agreement with those found experimentally. In Table I we summarize these results as a consistency test for our methodology. LAPW computations confirm the metallic character of these intermetallics. The total DOS plots for these compounds are sketched in Fig. 1, where the position of the 4f states are indicated when applies. The DOS exhibits essentially the same structure for the diamagnetic cases R=Y and La. It stands up the La-4f states appearing 3.5 eV above the Fermi energy. Y(La)-

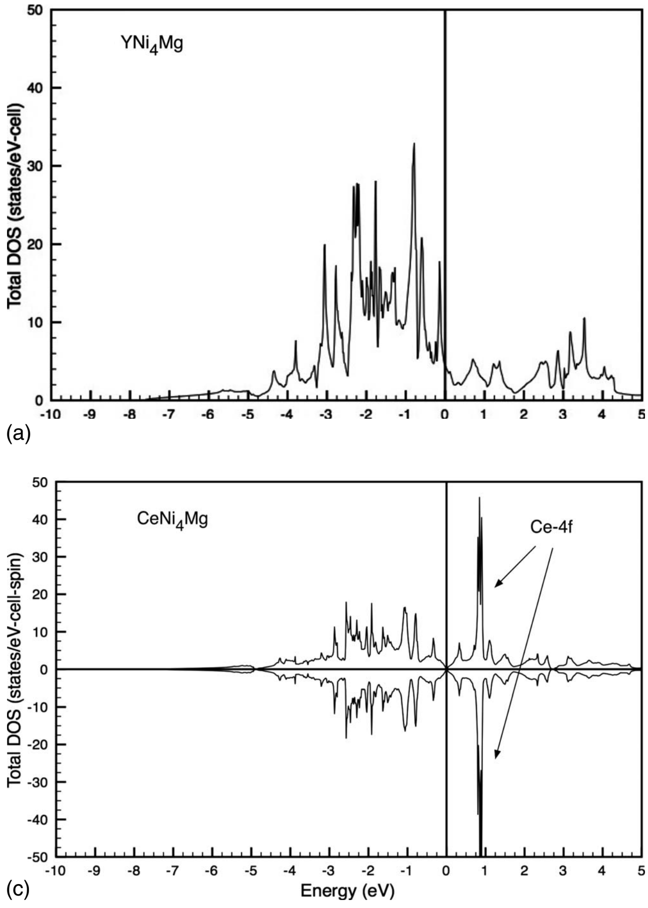

FIG. 1. Total density of states (states/eV cell) for $R\mathrm{Ni}_4\mathrm{Mg}$ (a) R=Y, (b) R=La, (c) R=Ce, and (d) R=Nd. The position of the 4f bands are indicated when applies. The energy origin is set to the Fermi level.

TABLE II. Identified interstitial sites in the $R\mathrm{Ni_4Mg}$ intermetallics. Site in the Wyckoff notation, position (in relative coordinates), radius (in Å) of the interstitial site, local coordination, and metal-hydrogen distances (in Å) $d_{\mathrm{HNi}}/d_{\mathrm{HMg}}$.

Wyckoff sites	Position	Radius	Coordination	$d_{\mathrm{HNi}}/d_{\mathrm{HMg}}$
$4b$	$\frac{1}{2},x,x$	0.38	$\mathrm{Ni_4}$	1.63
$4d$	$\frac{3}{4},x,x$	0.42	$\mathrm{Ni_4}$	1.67
$16e$	$0.387,x,x$	0.33	$\mathrm{Ni_3Mg}$	1.69/2.11

derived intermetallic shows a DOS at Fermi level of 4.47 (5.73) states/eV cell, where the most important contribution arises from the Ni-d states.

The Ce and Nd cases obviously exhibit differences owing to the nature of the rare earth. In the Ce-based compound, we found a small DOS at the Fermi energy (0.13 states/eV cell) and a zero magnetic moment for the compound. The Ni-d band is completely filled indicating a d^{10} configuration. The Ce-4f band is empty and appears at 0.85 eV above the Fermi level. We found this compound no magnetic. Geibel *et al.*[18] claim that $\mathrm{CeNi_4Mg}$ seems to be an intermediate-valence compound. Their magnetic-susceptibility measurements on this compound do not follow the Curie-Weiss law and is similar to other Ce-based compounds exhibiting a probable heavy-fermion behavior. In the Nd case we found a DOS at the Fermi energy (40.6/34.3 states/eV spin cell) similar to that computed for the Y and La compounds. The Ni-d band is almost filled being the major contribution at the Fermi energy. In this compound we observe a contribution of the Nd-4f states appearing in the valence band around 3 eV below the Fermi energy. The remaining unoccupied states spread in the conduction band, centered at 2 and 3.5 eV. The magnetic moment attain $2.9\mu_B$ and is localized in the Nd atom. This computed value is comparable with that obtained for the $\mathrm{Nd^{+3}}$ free cation and the magnetic moment on Nd in the $\mathrm{NdAl_2}$ Laves-phase compound[19] being $3.22\mu_B$. It is interesting to note that we didn't observe any spin polarization in the Ni atoms.

It is interesting to note that the Ce and Pr compounds exhibit small volume cells respect to the other lanthanides. These anomalies could indicate a high oxidation state (small cation size) for these elements in $R\mathrm{Ni_4Mg}$. The computation of the formation enthalpy for the intermetallic compounds clearly indicates the lower stability of the Ce compound respect to the other considered compounds. We found −230.84, −187.94, −51.45, and −193.24 kJ/mol for R=Y, La, Ce, and Nd in $R\mathrm{Ni_4Mg}$, respectively.

We have carried out geometry optimizations (PAW approach) for some disordered $R\mathrm{Ni_4Mg}$ (R=Y, La, and Nd) systems. For these compounds this substitutional disorder has been characterized or at least mentioned in literature. We considered a single Mg-Ni_I,[20] exchange in cells having the $R_4\mathrm{Ni_{16}Mg_4}$ and $R_{32}\mathrm{Ni_{128}Mg_{32}}$ stoichiometries. The energy difference between a single La-Ni exchange and the fully ordered system indicates that the substitutional disorder is not energetically favored. For the small cell (large exchange ratio) the obtained energy difference ranges from 0.34 to 0.36 eV/$R\mathrm{Ni_4Mg}$ while in the small exchange ratio (large cell) this energy difference remains positive and is also similar for the three compounds being 0.05 eV/$R\mathrm{Ni_4Mg}$. This low-exchange concentration seems to be the general case. For $\mathrm{NdNi_4Mg}$, Guénée *et al.*[4] found after Rietveld refinement of their accurate synchrotron powder-diffraction data that the exchange between Mg and Ni is just 0.088 atoms/$\mathrm{NdNi_4Mg}$. Our computations, for the small exchange concentration case, corresponds to 0.031 atoms/$\mathrm{NdNi_4Mg}$. Since both figures are of the same order of magnitude, we can assert that our positive-energy estimate for substitutional exchange can only be compensated by the configurational entropy term.

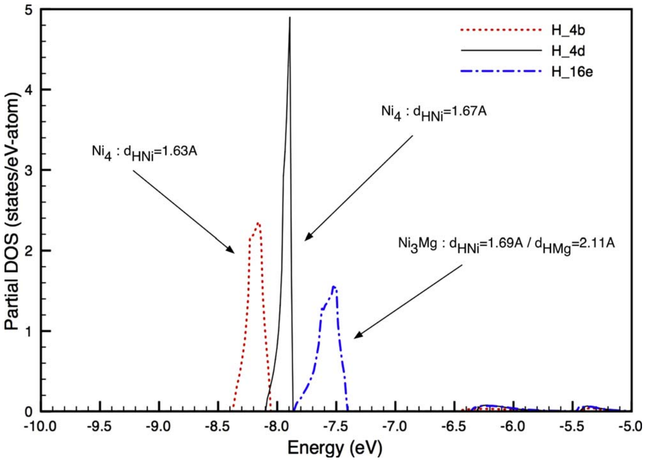

FIG. 2. (Color online) Partial density of states (states/eV atom) at the hydrogen occupied interstitial site in $[\mathrm{YNi_4Mg}]_n\mathrm{H}$ (n=32) system. The hydrogen position is identified by the Wyckoff symbol in accordance to Table II. The energy origin is set to the Fermi level.

B. The energetics of hydrogen insertion

In such kind of crystals it is possible to identify interstitial sites suitable to hydrogen insertion. We identified three of them having sizes close to the Westlake criteria,[21] (radius of the site larger than 0.4 Å). The identified interstitial sites are summarized in Table II. It is interesting to note that the full occupancy of these sites implies an overall H stoichiometry of 6 H/$R\mathrm{Ni_4Mg}$ which is larger than the experimentally found maximal H content capacity for these compounds. A detailed look of the site-site distances indicates that the 4b and 16e exhibit distances shorter than 2.1 Å, the H-H distance limit criteria established by Westlake.[21] This means that these sites should exhibit mutual blocking, regardless the energetic stabilization that a single H atom should exhibit when occupy a particular site. This effect also has a contribution in the early stage of the hydride formation—solid solution phase—diminishing the configurational entropy which strongly contributes to the solid solution-formation free energy.[22–25] The minimal H-H distance criteria is commonly followed by the majority of the intermetallic hydrides. It is important to note that the geometrical considerations developed by Westlake has been carried out in highly symmetric crystals. In recent years it has been shown experimentally[26] and investigated theoretically[27,28] that the

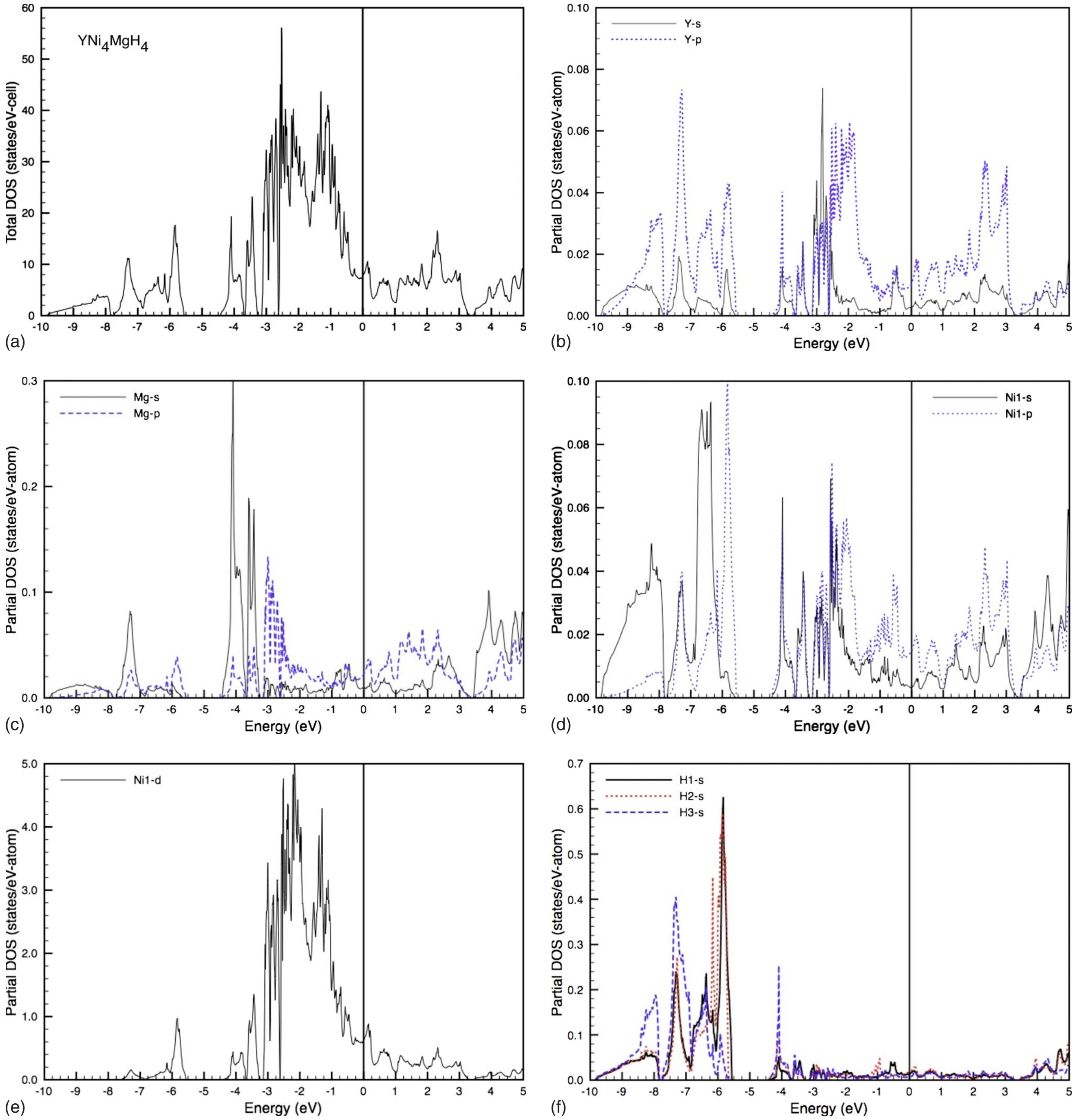

FIG. 3. (Color online) Total density of states (states/eV cell) and site-projected density of states (states/eV atom) for YNi_4MgH_4. (a) Total DOS, (b) partial DOS for Y-*s* and Y-*p* contributions. (c) Partial DOS for Mg atom, (d) Ni atom (*s* and *p* contributions), (e) Ni-*d* contribution, and (f) hydrogen sites (H_1, H_2, and H_3). The energy origin is set to the Fermi level.

violation of the minimal H-H distance criteria occurs in hydrides having low-symmetry and low-coordinated hydrogen sites. This family of rare-earth hydrides exhibits short Ni-H distances indicating strong interactions and the H atoms show a sizeable density-charge polarization due to the low symmetry and local coordination. In the present case, H occupy sites in the RNi$_4$Mg hydrides as indicated in Table II. These sites show high symmetry and coordination which prevent too short H-metal distances.

Thus, we investigated the energetic aspects of the hydrogen insertion in these systems as well as the details of the electronic-structure modifications in the early stages of hydrogenation. In order to compute the H-insertion energy (ϵ_H) in these compounds, we took as examples the cases of H in the above mentioned interstitial sites of YNi_4Mg and $LaNi_4Mg$ systems. The H-insertion energy corresponds to the general reaction $[RNi_4Mg]_n + H \rightarrow [RNi_4Mg]_n H$ where n is set by the size of the considered supercell. In these computation we used a $2\times2\times2$ supercell, making $n=32$. This choice makes large enough H-H distances in order to compute the single H-insertion situation. After a full-geometry optimization of the corresponding supercells (PAW approach) we proceeded to compute the all-electron electronic structure (LAPW approach). In Fig. 2 we show the partial DOS at the H site for the occupation of the three interstitials found sites in YNi$_4$Mg. The results obtained for La compound are similar. It is interesting to note that the nickel-hydrogen distance (Table II) correlates well with the position of the peak of the H-site DOS.

These results are consistent with the obtained ϵ_H being −0.13, −0.61, and −0.55 eV/H for the H_{4b}, H_{4d}, and H_{16e} hydrogen insertion. It is also interesting to note that one of the Ni fourfold coordinated sites (4b) exhibits a stabilization energy well above to those of the also fourfold coordinated Ni$_4$ and Ni$_3$Mg sites. The H_{4b} site seems to exhibit too short Ni-H distances avoiding the necessary relaxation to accommodate the H atom. This makes this site less energetically favored. The energetically preferred occupancy of the 4d and 16e sites should indicate a Ni-H distance threshold. However, these sites should exhibit mutual structural blocking for occupation.

C. Hydride compounds

The geometry optimization of the ordered full-stoichiometric hydrides RNi$_4$MgH$_4$ have been obtained at PAW theory level. We found an excellent agreement with the available experimental data; in particular, for the NdNi$_4$MgH$_4$ case. The all-electron electronic structures have also been computed. The total as well as partial DOS for YNi$_4$MgH$_4$ are plotted in Fig. 3. The total DOS exhibits the expected structure for a complex metal hydride. At the bottom of the energy scale, it can be observed the Ni-d,s/H-s bonding states, consistent with the partial DOS contributions plotted in Figs. 3(d)–3(f). In particular, it is interesting to note that the H-s states are located in the energy range of the PDOS of diluted hydrogen in the intermetallic matrix (Fig. 2). The contributions to the DOS arising from Y and Mg are small as expected for electron-donor elements. This general features of the electronic structure of YNi$_4$MgH$_4$ are also present in the La-, Ce-, and Nd-based hydrides. The total DOS for these compounds are plotted in Fig. 4, where we observe the specific details owing to the position of the R-4f band. In all the hydrides investigated, we found a metallic behavior with a Fermi energy DOS comparable to that of the parent intermetallic. As in the intermetallic parent compounds, the main contributions to the DOS at the Fermi level arise from the Ni-d states. The Y and La compounds are found diamagnetic with a DOS at Fermi level of 7.64 and 7.91 states/eV cell, respectively. The Ni-d contributions are similar for the three nonequivalent Ni atoms being close to 9.5 states/eV atom. In the Ce and Nd cases, the values of the total DOS and Ni-d PDOS at the Fermi energy are similar to those found for Y and La. Ce- and Nd-derived hydrides appear to be magnetic with a local magnetization of 0.94 and 2.93μ_B per Ce and Nd, respectively. The positions of the 4f bands are indicated in the Fig. 4. The appearance of a Ce-4f magnetic moment in the hydride contrasts with the diamagnetic behavior observed in the corresponding intermetallic.

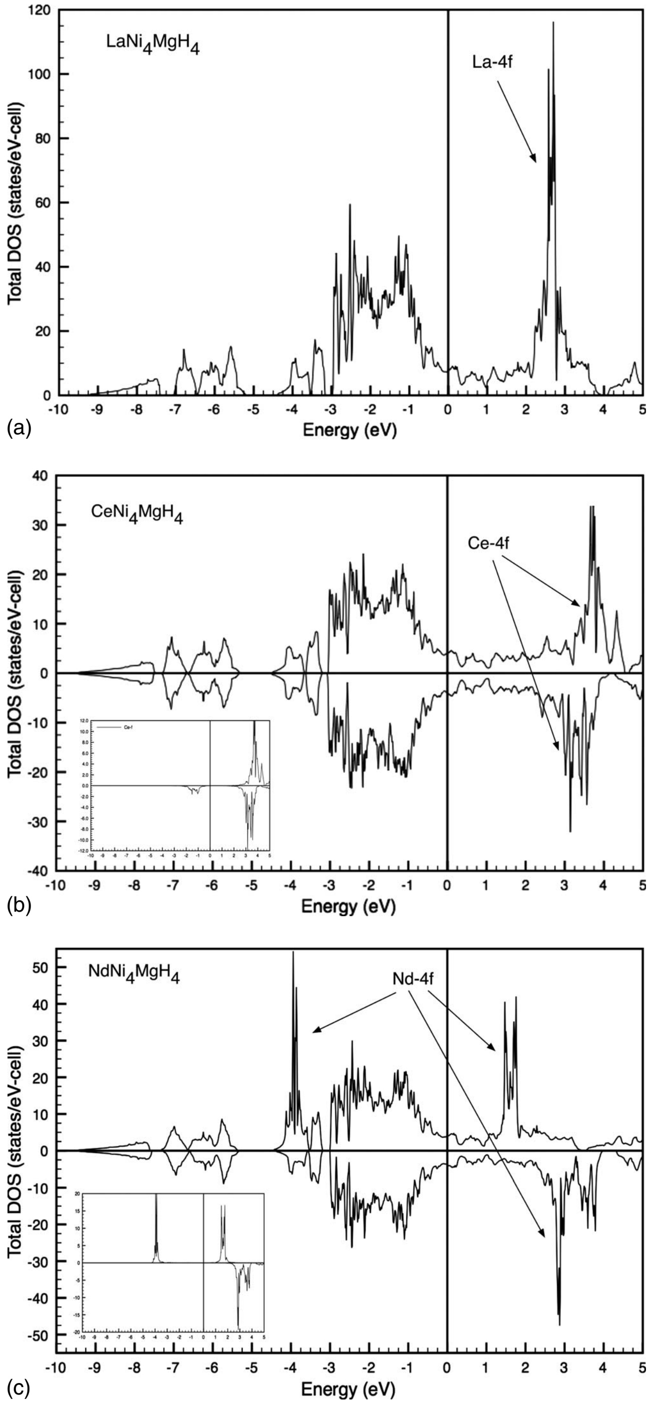

FIG. 4. Total density of states for (a) LaNi$_4$MgH$_4$ (in states/eV cell), (b) CeNi$_4$MgH$_4$, and (c) NdNi$_4$MgH$_4$ (in states/eV cell spin). The position of the rare-earth 4f states are indicated. The insets show the partial DOS for the rare-earth 4f contributions. The energy origin is set to the Fermi level.

These hydrides exhibit a reduction in symmetry exhibiting a $Pnm2_1$ orthorhombic space group. As a consequence, the local symmetry of the H-atomic sites is lower when compared to the interstitial sites identified in the intermetallic matrix. We computed the H-vacancy-formation energy (ϵ_V) for each of the three occupied H sites (H_1-4b, H_2-2a, and

TABLE III. Structural details of the H sites in $NdNi_4MgH_4$ hydrides.

H type	Wyckoff sites	Position	Coordination
H1	4*b*	0.746, 0.509, 0.754	Ni_2MgNd_2
H2	2*a*	0, 0.716, 0.513	Ni_2MgNd_2
H3	2*a*	0, 0.946, 0.825	Ni_3Nd

H_3-2*a*, see Table III,[20]). The H-vacancy formation energy was computed after the reaction $[RNi_4MgH_4]_n \rightarrow [[RNi_4Mg]H_{4-(1/n)}]_n + H$. The n value depends again on the size of the supercell ($n=32$). We found that ϵ_V attains the high values 0.82, 0.73, and 0.85 eV/H for the H_1-4*b*, H_2-2*a*, and H_3-2*a* in $NdNi_4MgH_4$ hydride. These figures are similar for all the RNi_4MgH_4 hydrides. It is interesting to note that the refinement of the neutron-powder diffraction on $Nd_4MgH_{3.6}$, a slightly substoichiometric hydride, indicates that the occupancy of the three H sites is essentially the same: 0.92, 0.89, and 0.90 for H_1, H_2, and H_3, respectively. This experimental occupancy ratio indicates that the three H sites behave in a similar way when hydrogen is withdrawn. This is in line with our findings for the H-vacancy formation energy cost since we obtain very similar values for the three sites.

The computation of the formation enthalpy for the RNi_4MgH_4 hydrides yield −298.18, −284.38, −94.39, and −276.29 kJ/mol for $R=$Y, La, Ce, and Nd, respectively. As we found for the intermetallic, the hydride formation enthalpy for the Ce compound is anomalously small compared to the other rare earths. This is consistent with the recent work of Roquefere *et al.*[6,7] since $CeNi_4Mg$ decomposes into $CeH_{2.5}$ and other subproducts under hydrogenation. The small hydride-formation enthalpy allows other parasitic reactions to take place.

IV. CONCLUSIONS

We have investigated the electronic structure of a series of intermetallic compounds known for their ability to absorb hydrogen up to high concentrations and precipitate a hydride phase. The reference intermetallics are found, as expected, of metallic behavior. The computation of the electronic structure and energetics of hydrogen inclusion in selected interstitial sites, indicates that clear differences for preferred occupation exist. We found that, besides the blocking-site effect (geometrical effect) between the H_{4d} and H_{16e} interstitial sites, these are energetically preferred respect to H_{4b}. These results are consistent with details of the H density of states band as well as the obtained equilibrium metal-H distances. In the hydride phase, we have found that the experimentally three determined H-sites exhibit similar H-vacancy energies. This indicates that the symmetry reduction respect to the original intermetallic favors the site relaxation, making all the H atoms energetically equivalent.

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