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Ab initio study of the hydrogenation properties of Mg-based binary and ternary compounds Mg_2X ($X = Ni$, Si) and $YMgNi_4$

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Abstract

In this paper the results of ab initio electronic structure investigations of several Mg-based compounds are presented. From our total energy calculations and from the analysis of the electronic factors that control the stability of the intermetallic compounds and their hydrides, we show why Mg_2NiH_4 is stable while Mg_2Si does not absorb hydrogen. Our results are in agreement with recent experimental data on the hydrogenation of Mg_2X phases ($X = Ni$, Si, Ge, Sn) of Janot et al., as well as with studies of the role of Si in the destabilization of MgH_2 through the formation of Mg_2Si, by Vajo et al.

We have also analyzed the structural and electronic properties of one of the cubic $SnMgCu_4$-type structure ternary compound, $YMgNi_4$, recently synthesized and of its hydride $YMgNi_4H_4$. For the hydride, we predict that the $Pmn2_1$ structure is more stable than a cubic structure. The calculated enthalpy of formation of the hydride, −37.7 kJ/mol H_2 is in good agreement with the experimental data, −38.5 kJ/mol H_2 of Aono et al.

Keywords: Hydrogen absorbing materials; Metal hydrides; Electronic band structure; Electronic properties

1. Introduction

Extensive research effort has been devoted to the hydriding properties of Mg-based alloys. One of the crucial goals being to maintain a high massic hydrogen storage capacity while forming hydrides less stable than MgH_2. One of the routes explored to obtain hydrogen storage materials suitable for mobile applications has been to search for alloys of magnesium with elements having a low affinity for hydrogen. Reilly and Wiswall [1] showed that Mg_2Ni absorbs reversibly hydrogen with a lower, but still too high, desorption temperature. More recently, extensive research has been conducted on light alloys. Mechanical alloying (MA) techniques including reactive MA (RMA) under hydrogen atmosphere have been successfully used to improve the hydrogen absorption and desorption kinetics of magnesium [2,3], Mg_2Ni [4–6], magnesium aluminium alloys. An important effort has been made to improve the MA and RMA results by incorporation of simple metals (Al, Li) [4], transition elements [4,7,8] and intermetallic compounds [9].

Another strategy has been explored recently [10,11] that consists of destabilizing the too stable ionic metal hydrides LiH and MgH_2 by elements such as Si [10], or Ge [11], via the formation of Li_xSi or Mg_2Si [10] or Mg_2Ge [11], upon dehydrogenation. Motivated by the recent experimental data on the hydrogenation of Mg_2X phases ($X = Ni$, Si, Ge, Sn) of Janot et al. [13], the controversy on the possible hydrogen absorption by Mg_2Si [12], as well as by studies of the role of Si in the destabilization of MgH_2 through the formation of Mg_2Si [10], we performed ab initio electronic structure investigations of several Mg-based compounds using an ab initio method. We show why Mg_2NiH_4 is stable while Mg_2Si does not absorb hydrogen.

We have also investigated the hydrogenation properties of a ternary compound $YMgNi_4$ that belongs to a series of ternary intermetallic compounds $AMgNi_4$ (A = Y, Ca, La, Ce, Pr, Nd), recently explored experimentally in several groups [14–17]. This series of compounds could be of interest for hydrogen storage applications since Aono et al. [14] found that in the case of $YMgNi_4$, the reversible hydrogen capacity is ∼1.05 wt% and the thermodynamic properties are comparable to those of the $LaNi_5$–H system.

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2. Approach

We have performed density-functional calculations of the electronic properties of Mg-based binary and ternary compounds Mg_2X (X = Si, Ni), $YMgNi_4$ and their hydrides. These calculations were done using the full potential linearized augmented plane-wave (FPLAPW) method [18]. Well-converged basis sets of LAPW functions were employed. Additional local orbitals were used to treat the high-lying semicore states of metal atoms and to relax linearization errors [19]. Convergence tests were performed as a function of the number of **k** points in the irreducible wedge of the Brillouin zone in order to get converged values of the total energies to better than 0.1 mRy. For Mg_2SiH_4 and Mg_2NiH_4, the total energies have been calculated as a function of the lattice parameter as well as a function of the X–H distances (X = Si, Ni) assuming a tetrahedral configuration of the H atoms around X.

In the case of the hydride $YMgNi_4H_4$, since structural determinations are not yet available to our knowledge, the structure was determined within the $Pmm2_1$ space group [16] by relaxing all the internal coordinates as well as the cell shape and cell volume.

3. Results

3.1. Hydrogenation properties of the binary compounds Mg_2X (X = Si, Ni)

Guinet et al. [12] claimed that Mg_2Si can absorb 2 wt% of hydrogen after 10 h at 300 °C, while recent studies on Mg_2X phases (X = Si, Ge, Sn) prepared by powder metallurgy and ball-milling showed that Mg_2Si does not absorb hydrogen; it rather decomposes into Si and MgH_2 when ball-milled under hydrogen atmosphere [13].

We thus considered the possibility of hydrogen absorption by Mg_2Si. The silicide cristallizes within the antifluorite cubic structure (space group $Fm\text{-}3m$) in which the Si atoms form an fcc lattice and the Mg atoms located at the (1/4,1/4,1/4) positions form a simple cubic lattice. The minimization of the total energy as a function of the lattice parameter resulted in a calculated value of 11.83 a.u. in satisfactory agreement with the experimental value, $a = 12$ a.u. [20]. The total density of states (DOS) plotted in Fig. 1 shows that the silicide, in agreement with experimental findings and previous band structure calculations [21,22], is a small gap semi-conductor. The first rather narrow band centered around −8 eV corresponds to the Si-3s band slightly hybridized with Mg s and p states. This band is separated by a gap from the next three Si-3p bands hybridized with Mg s and p states. Since the silicide has eight valence electrons, the first four bands are filled, they are separated by an indirect energy gap of 0.3 eV between the Γ and X points of the fcc Brillouin zone, from the conduction band states. Due to the difference in electronegativity between Mg and Si, the essential part of the Mg-s, p states are empty and located above the energy gap.

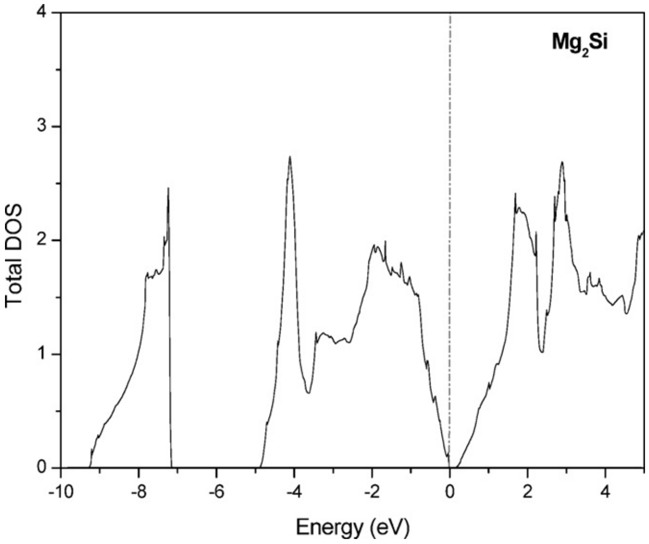

Fig. 1. The total density of states (states/eV formula unit) of Mg_2Si. The origin of energies is chosen at the top of the valence band.

The calculated formation energy of the silicide obtained by subtracting from the total energy of the silicide, the energies of silicon and magnesium in their solid state form is ΔH_f (Mg_2Si) = −70 kJ/mol. This calculated result is in satisfactory agreement with the experimental value, −77.8 kJ/mol [10].

We considered the possible formation of a hydride Mg_2SiH_4 assuming that the metal sublattice retains the cubic antifluorite structure. For the H atoms, by analogy with the silane SiH_4 molecule, we assumed a tetrahedral configuration around Si. Since hydrogen absorption leads usually to lattice expansion, we varied the lattice parameter, a, and also the Si–H distance ($d_{Si\text{–}H}$ = 2.8 a.u. for the silane molecule) in a broad range. The energy surface plotted in Fig. 2 as a function of a and $d_{Si\text{–}H}$ is found to be fully dissociative, it does not present any minimum, indicating that the hydride under study is not stable. We also considered other geometries for the SiH_4 units. Keeping the Si–H

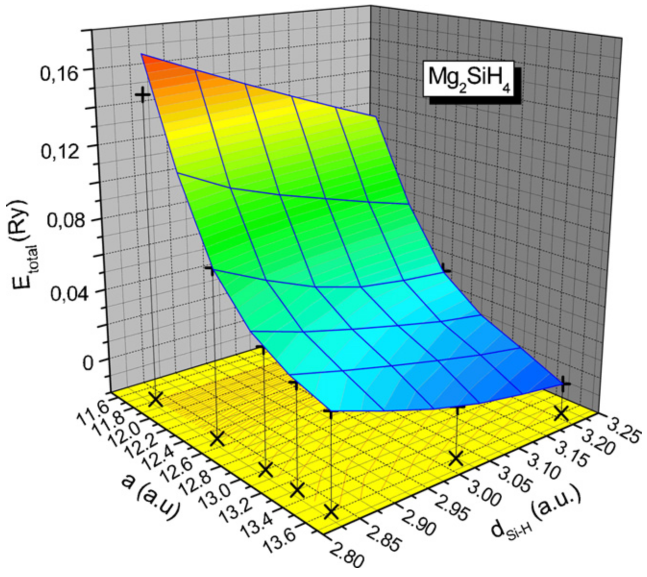

Fig. 2. The total energy surface of Mg_2SiH_4 is plotted vs. the lattice parameter of the cubic cell, a, and vs. the Si–H distance, $d_{si\text{–}H}$.

distance fixed, we flattened progressively the SiH_4 tetrahedron up to a square planar configuration. In all cases, the formation energy of the hydride calculated by subtracting from the total energy of the hydride, the energy of the silicide and the energy of two H_2 molecules was found to be largely positive and greater than 90 kJ/mol H_2 for all the configurations tried, indicating that the corresponding hydrides are not stable.

Our results are consistent with the experimental results of Janot et al. [13] who found that ball milling Mg and Si powder in the Mg_2Si proportions under hydrogen atmosphere does not result in hydrogen absorption, in contradiction with previous claims [12].

In order to understand the microscopic origin of this result, we analyzed the total DOS of Mg_2SiH_4 plotted in Fig. 3. The first two structures observed in the total DOS correspond to bonding states of hydrogen, respectively, with Si-3s and -3p states, hybridized with Mg-s, p orbitals. As in Mg_2Si, these four bands are filled. Since these are mostly associated with the Si–H covalent bonding interaction, they are stabilized in energy compared to the intermetallic. As a result, the energy gap separating the Mg-s, p and antibonding Si–H sates increases from 0.3 to 4.16 eV. Since the hydride has 12 valence electrons, the Fermi level falls above the wide gap in the DOS structure associated with the antibonding states, a situation highly unfavourable for the formation of a stable hydride.

Since the enthalpy of formation of MgH_2 is −75 kJ/mol H_2, while the calculated formation energy of Mg_2Si is −70 kJ/mol, in the presence of Si, as found by Vajo et al. [10], MgH_2 is expected to cycle according to the reaction:

$$MgH_2 + 1/2Si \rightarrow 1/2Mg_2Si + H_2$$

The calculated energy of the above reaction, resulting in the release of an H_2 molecule, is 40 kJ, in satisfactory agreement with the experimental value of 36.4 kJ [10]. This should correspond to a desorption temperature lower than that obtained for the reaction of formation of MgH_2 from the elements. However, it is to be noted that, in the presence of Si, the hydrogen absorption capacity is reduced from 7.6 to 5 wt% [10].

In order to understand the origin of the differences in the hydrogen absorption properties of Mg_2Si and Mg_2Ni, we studied the hydride Mg_2NiH_4. In their pioneering work, Reilly and Wiswall [1] showed that the intermetallic compound Mg_2Ni, of hexagonal structure absorbs reversibly hydrogen and forms a stable hydride phase β-Mg_2NiH_4 with a massic capacity of 3.6 wt% and a desorption temperature of 523 K, still too high for mobile applications. Neutron scattering data [23–25] showed that above 508 K, the hydride has a cubic structure (space group *Fm*-3*m*) with a lattice parameter $a = 12.294$ a.u. At lower temperature, a slight distortion of the cubic structure leads to a monoclinic phase. In the cubic phase, high resolution neutron diffraction data [23] indicate that the H atoms form quasi regular tetrahedra around the Ni atoms, the Ni–H distances are short, 2.778 a.u., leading to quasi-molecular weakly interacting NiH_4 entities. We studied the high temperature cubic phase Mg_2NiH_4 in which the cubic antifluorite structure metal sublattice is isostructural to that of Mg_2Si.

Following the same procedure as that described above for Mg_2SiH_4, we varied the lattice parameter, a, and the Ni–H distance, d. The corresponding total energy surface plotted in Fig. 4 presents a minimum for $a = 12.50$ a.u. and $d = 2.83$ a.u., contrary to the result obtained for the energy surface of Mg_2SiH_4. These calculated values of a and d are in good agreement with the neutron data.

The total DOS of Mg_2NiH_4 is plotted in Fig. 5. The first structure located between −9.5 and −6.7 eV corresponds to one band resulting from an interaction between the H-s, Ni-s and Mg-s, p states, while the second structure located between −6.7 and −4.3 eV corresponds to three bonding Ni-d, H-s bands. These four low energy bands associated with the metal–hydrogen bonding in the NiH_4 units are filled and separated by a gap of ∼1.75 eV from the next manifold of the five non-bonding Ni-d

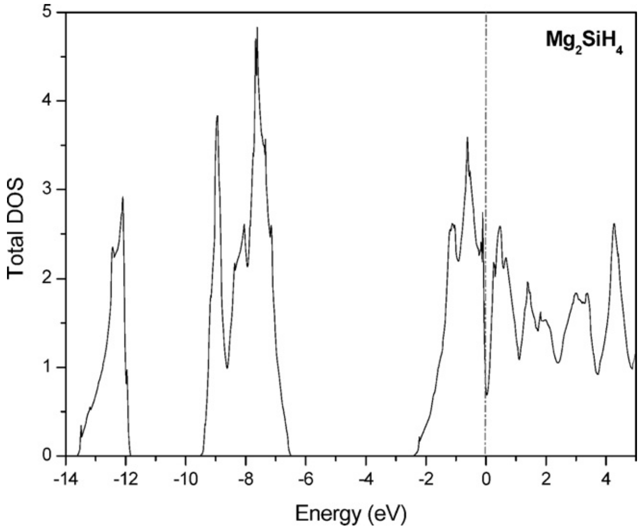

Fig. 3. The total density of states (states/eV formula unit) of Mg_2SiH_4. We assumed an antifluorite Mg_2Si sublattice with $a = 12.5$ a.u. and the H atoms in perfect tetrahedral configuration around Si, as in silane $S1H_4$ molecule, $d_{Si–H} = 2.8$ a.u. The origin of energies is chosen at the Fermi energy.

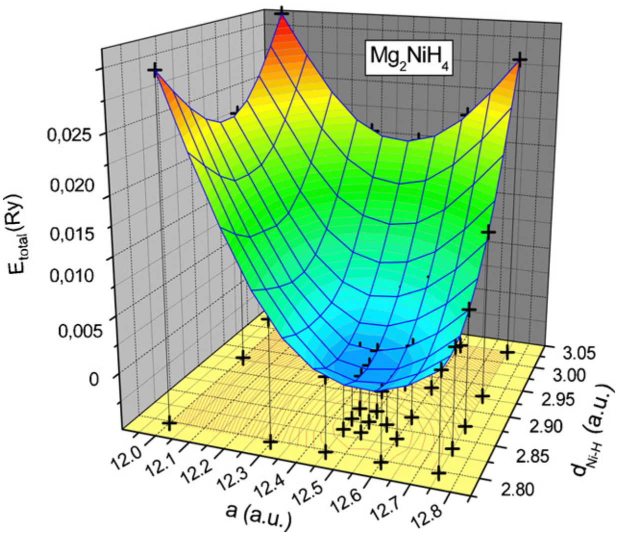

Fig. 4. The total energy surface of Mg_2NiH_4 is plotted vs. the lattice parameter of the cubic cell, a, and vs. the Ni–H distance, $d_{Ni–H}$.

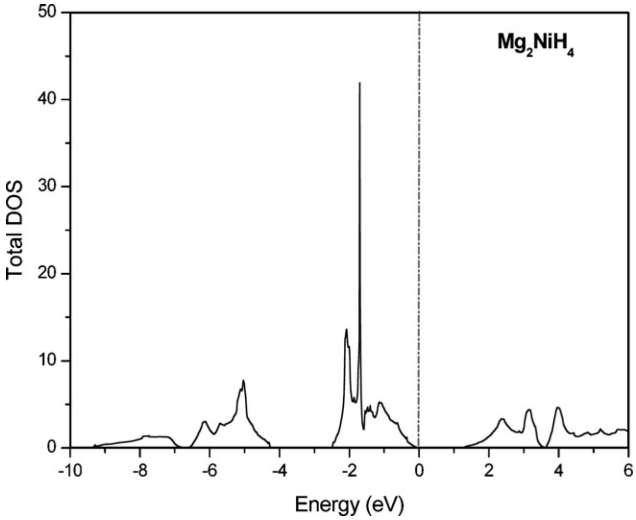

Fig. 5. The total density of states (states/eV formula unit) of Mg_2NiH_4. The origin of energies is chosen at the top of the valence band.

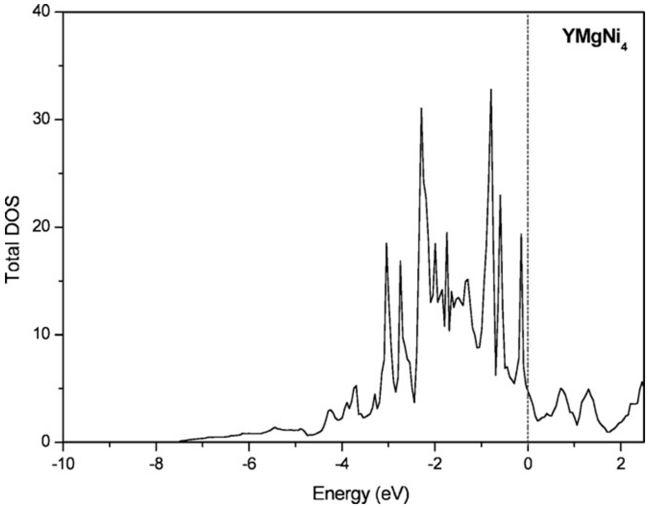

Fig. 6. The total density of states (states/eV formula unit) of $YMgNi_4$. The origin of energies is chosen at the Fermi energy.

bands that are fully occupied since the hydride counts a total of 18 valence electrons. An energy gap of ~1.4 eV separates the nine occupied valence bands from the higher energy Mg-s, p and antibonding Ni–H states, conferring to the material semi-conducting properties, in agreement with experimental findings. The transition from a metallic state of the intermetallic Mg_2Ni to a semi-conducting state of the hydrogen-loaded compound has been extensively studied for a possible application as switchable mirror [26].

This hydride is characterised by important covalent intramolecular Ni–H interactions inside the NiH_4 cages, while the direct interaction between the molecular entities is very weak. The formal charge of the NiH_4 cages is 4−, the interaction with Mg is essentially ionic.

It is the filling of the Ni–H bonding and Ni-nonbonding states by 18 valence electrons that confer to the hydride its stability [27–30]. Mg_2NiH_4 belongs to a series of isovalent stable hydrides Mg_2FeH_6, Mg_2CoH_5 that obey the 18 valence electrons rule. In this series of compounds, the maximum hydrogen absorption capacity increases when the atomic number of the transition element decreases.

The calculations performed explain on a microscopic basis why Mg_2Ni forms a stable hydride Mg_2NiH_4 and strongly suggest that Mg_2SiH_4 does not form.

3.2. Structural and electronic properties of $YMgNi_4$ and $YMgNi_4H_4$

The structural and hydriding properties of Mg-based ternary intermetallic hydrides have recently been investigated by several groups. This series of compounds can be of interest for hydrogen storage applications since Aono et al. found that in the case of $YMgNi_4$, the reversible hydrogen capacity is ~1.05 wt% and the thermodynamic properties are comparable to those of the $LaNi_5$–H system.

Powder diffraction data analysis showed that the $AMgNi_4$ compounds (A = Y, La, Ce, Nd, etc.) crystallize within the cubic $SnMgCu_4$ structure (space group *F*-43*m*) This structure that can also be viewed as an order derivative of the cubic $AuBe_5$ type structure is closely related to the cubic AB_2 Laves phase. The Y atoms form an fcc sublattice, they occupy the (4*a*: 0,0,0) sites; while the tetrahedral sites (4*c*: 1/4,1/4,1/4), are occupied alternatively in an ordered way by Mg atoms and Ni_4 tetrahedra. The density of states plotted in Fig. 6 shows that the occupied states are dominated by the Ni-3d bands of width ~4 eV, hybridized with broad Y-4d sates and with the s–p states of Mg, Ni and Y. The Ni-d states are almost filled and the compound is found to be metallic with a rather low value of the DOS at the Fermi energy, E_F. The main parts of the Y-4d states are located above E_F. These results show that this intermetallic cannot be considered as a simple charge transfer compound. A minimization of the total energy as a function of the volume led to a calculated lattice parameter $a = 7.0149$ Å, a value in excellent agreement with the experimental data of Aono et al. [14], $a = 7.01$ Å, and Paul-Boncour [31], $a = 7.008$ Å, while Kadir et al. [15] reported a much larger value, $a = 7.1853(3)$ Å.

The hydride $YMgNi_4H_4$ was also investigated. Since, to our knowledge no structural data exist for this compound, we considered two possible crystal structures. Following the synchrotron and neutron powder diffraction data of Guénée et al. [16] on deuterated $NdNi_4MgD_{3.6}$, we used an orthorhombic lattice with space group $Pmn2_1$ in which Y and Mg occupy 2*a* sites. Three types of Ni and H atoms occupy, respectively, 2*a*, 2*a* and 4*b* sites. Two H atoms are coordinated by trigonal bipyramids (A_2B_3 base: B = 2Ni, Mg; apices: A = 2Y) and one H is coordinated by a tetrahedron (AB_3, A = Y, B = 3Ni). In our calculation, we relaxed the internal coordinates of the metal and H atoms as well as the volume and cell shape. The calculated lattice parameters are $a = 5.0033$ Å, $b = 5.4296$ Å, $c = 7.2548$ Å. This corresponds to a calculated relative volume expansion $\Delta V/V = 14.2\%$ from the intermetallic to the hydride, a value of the same order of magnitude as that observed for hydrides of $SnMgCu_4$ type structure.

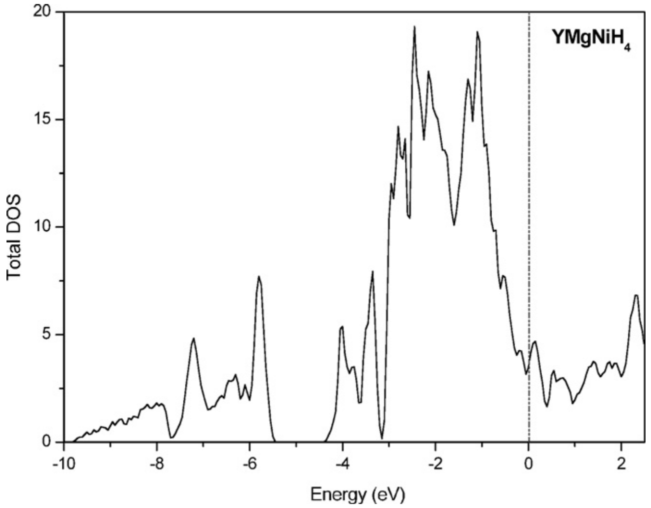

Fig. 7. The total density of states (states/eV formula unit) of $YMgNi_4H_4$. The origin of energies is chosen at the Fermi energy.

The density of states plotted in Fig. 7 shows that the hydride is characterised by the presence of four metal–H bonding bands centred around 7 eV below E_F. H interacts mostly with the Y-4d and Ni-3d states as well as with the s, p states of Mg, Y, Ni. The position of the Fermi level of the hydride is similar to that of the intermetallic, at the top of the almost filled Ni-d states hybridized with the Y-4d states. The DOS at E_F remains low as in the intermetallic. The stability of the hydride results from the stabilisation of metal states due to the metal–hydrogen bonding as well as with the absence of notable shift of the Fermi level towards higher energies upon formation of the hydride.

Within this structure, from the difference in the calculated total energies, we find this hydride to be stable. We obtained a formation enthalpy of the hydride of −37.7 kJ/mol H_2, a value in very good agreement with the experimental data of Aono et al. [14], −38.5 kJ/mol H_2.

We have also considered for the hydride, a possible metal sublattice with the cubic structure of $SnMgCu_4$ type and an ordered occupancy of $YMgNi_2$ sites (corresponding to the A_2B_2 site occupancy often observed in AB_2 Laves phase compounds. Within this structure, the total energy could be minimized as a function of the lattice parameter. However, the calculated value of the formation enthalpy of the hydride was found to be only −3.3 kJ/mol H_2. This value indicates that in this structure, the hydride is nearly unstable. The $Pmn2_1$ structure has been found to be the more stable of the two structures considered for $YMgNi_2H_4$.

4. Conclusions

In this work, we have shown that Mg_2Si cannot form a concentrated hydride of composition Mg_2SiH_4 isostructural to the cubic phase Mg_2NiH_4. We find the reaction enthalpy of such hypothetical hydride to be highly positive, the energy surface as a function of lattice parameter and Si–H distances does not present a minimum, it is rather fully dissociative. We explain on a microscopic basis why Mg_2NiH_4 is stable while our results strongly suggest that Mg_2SiH_4 cannot be formed. In contrast to the claims of Guinet et al. [12], our results are in agreement with recent experimental data on the hydrogenation of Mg_2X phases (X = Ni, Si, Ge, Sn) of Janot et al. [13], as well as with studies of the role of Si in the destabilization of MgH_2 through the formation of Mg_2Si by Vajo et al. [10].

We calculated the structural and electronic properties of the recently synthesized ternary intermetallic $YMgNi_4$, and of its hydride $YMgNi_4H_4$. For the hydride, we predict that the $Pmn2_1$ structure is more stable than a cubic structure. The calculated enthalpy of formation of the hydride, −37.7 kJ/mol H_2 is in good agreement with the experimental data, −38.5 kJ/mol H_2 of Aono et al. [14].

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References

[1] J.J. Reilly, R.H. Wiswall, J. Inorg. Chem. 7 (1968) 2254.
[2] J. Huot, E. Akiba, T. Takada, J. Alloys Compd. 231 (1995) 815.
[3] P. Tessier, H. Enoki, M. Bououdina, E. Akiba, J. Alloys Compd. 268 (1998) 285.
[4] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Compd. 217 (1995) 245.
[5] S. Orimo, H. Fujii, J. Alloys Compd. 232 (1997) L16.
[6] L. Aymard, M. Ichitsobo, M. Uchida, K. Sekreta, K. Ikazaki, J. Alloys Compd. 259 (1997) 5.
[7] Y. Tsushio, H. Enoki, E. Akiba, J. Alloys Compd. 281 (1998) 301.
[8] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, J. Alloys Compd. 291 (1999) 295.
[9] H. Reule, M. Hischer, A. Weiβhardt, H. Kronmüller, J. Alloys Compd. 305 (2000) 246.
[10] J.J. Vajo, F. Mertens, C.C. Ahn, R.C. Bowman Jr., B. Fultz, J. Phys. Chem. B 108 (2004) 13977.
[11] F.C. Gennari, F.J. Castro, G. Urretavizcaya, G. Meyer, J. Alloys Compd. 334 (2002) 277.
[12] P. Guinet, P. Perroud, J. Rebière, Hydrogen Energy System, Veziroglu-Seifritz, 1978.
[13] R. Janot, F. Cuevas, M. Latroche, A. Percheron-Guégan, Intermetallics 14 (2006) 163.
[14] K. Aono, S. Orimo, H. Fujii, J. Alloys Compd. 309 (2000) L1.
[15] K. Kadir, D. Noréus, I. Yamashita, J. Alloys Compd. 345 (2002) 141.
[16] L. Guénée, V. Favre-Nicolin, K. Yvon, J. Alloys Compd. 348 (2003) 129.
[17] Z.M. Wang, H.Y. Zhou, G. Cheng, Z.F. Gu, A.B. Yu, J. Alloys Compd. 384 (2004) 279.
[18] D.J. Singh, Planewaves Pseudopotentials and the LAPW Method, Kluwer Academic, Boston, 1994;
D.J. Singh, L. Nordstrom, Planewaves Pseudopotentials and the LAPW Method, 2nd ed., Springer, 2006.
[19] D.J. Singh, Phys. Rev. B 43 (1991) 6388.
[20] R.W.G. Wyckoff, Crystal Structures, vol. 1, 2nd ed., Interscience, New York, 1963, p. 241.
[21] D.M. Wood, A. Zunger, Phys. Rev. 34 (1986) 4105.
[22] J.L. Corkill, M.L. Cohen, Phys. Rev. B 48 (1993) 17138.
[23] P. Zolliker, K. Yvon, J.D. Jorgensen, F. Rotella, Inorg. Chem. 25 (1986) 3590.

[24] D. Noréus, P.E. Werner, J. Less Common Met. 97 (1984) 215.
[25] J.L. Soubeyroux, D. Fruchart, A. Mikou, M. Pezat, B. Darriet, Mater. Res. Bull. 19 (1984) 1119.
[26] T.J. Richardson, J.L. Slack, R.D. Armitage, R. Kostecki, B. Farangis, M.D. Rubin, Appl. Phys. Lett. 78 (2001) 3047.
[27] M. Gupta, J. Less-Common Met. 101 (1984) 35.
[28] G.N. Garcia, J.P. Abriata, J.O. Sofo, Phys. Rev. B 59 (1999) 11746.
[29] W.R. Myers, L.W. Wang, T.J. Richardson, M.D. Rubin, J. Appl. Phys. 91 (2002) 4879.
[30] U. Häussermann, H. Blomqvist, D. Noréus Inorg. Chem. 41 (2002) 3684.
[31] V. Paul-Boncour, private communication.