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Hydrogen storage in MgX ($X = \text{Cu}$ and Ni) systems - is there still news?

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Abstract

Among lightweight materials, magnesium-containing systems are of interest for hydrogen storage. Here, we use an efficient prediction scheme at *ab initio* level in order to identify new magnesium-based alloys that are stable under elevated pressure. The calculations show that pressure can radically change the minimum energy compositions and various new Mg-rich compounds were found under these conditions. For these Mg-rich compounds, a careful investigation and a search for potential hydrides was carried out and our study on the electronic properties reveal interesting information on the behavior of hydrogen atoms. Our theoretical investigations are in good agreement with very recent experimental results and demonstrate a possibility to identify destabilized metal hydrides. Consequently, the present result encourage the use of similar prediction schemes in order to identify and design destabilized systems for hydrogen storage applications.

Keywords: Hydrogen storage, Magnesium based alloy, Metal hydrides, DFT prediction, Evolutionary algorithm

1. Introduction

Currently, environmental and political concerns regarding global warming and the search for alternative fuels greatly impact scientific research. As a consequence, hydrogen technology, which promises green energy producing only water as combustion product, is of great interest and highly efficient hydrogen fuel cells already exist [1]. However, despite many years of research - except for a few pilot projects - hydrogen technology has still not been established as a broadly used technology in the renewable energy sector.

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This is mainly because the requirements for an effective, safe and reliable way to store hydrogen are not yet met. Next to storage in gas containers under high pressure, solid storage in form of metal hydrides seems to be one of the most promising options, because it is intrinsically safe and allows a volumetric capacity higher than liquid and compressed hydrogen and, all the more reason, it can operate at low pressure [2]. Recently, a lot of attention has been paid to novel solid state hydrogen storage systems, such as nano-structured materials [3] and Liquid Organic Hydrogen Carriers (LOHCs) [4, 5]. However, these methods still suffer from significant drawbacks and further developments remain challenging [6]. Thus, research on metal hydrides, such as MgH_2 , LiH and new ternary and quaternary alloys, is still ongoing and light-weight and reversible systems are intensively searched for. The use of hydrogen as a fuel would be convenient, because the only combustion product is water, no other exhaust fumes, that might be possibly toxic or detrimental for the climate, are emitted. Light metals, such as magnesium, are of particular interest due to their high gravimetric hydrogen density. However, their use remains limited because of their high thermodynamic stability and their slow dehydrogenation kinetics. Several ways to overcome this problem have been proposed, such as the use of solid solutions of hydride and fluoride [7, 8] or the use of magnesium-based alloys [9, 10, 11, 12]. For instance, in the system magnesium-nickel, it is known that the intermetallic compound Mg_2Ni shows a lower desorption temperature and improved hydrogenation kinetics [13, 14]. However, the disadvantage of this system is the low hydrogen storage capacity that is less than 4 %wt. It is also worth noting that the synthesis technics such as ball milling, infiltration in nano-scaffold and the use of selected additives can also influence the hydrogenation and dehydrogenation kinetics [15].

Recently, a new material, MgNi_3 , which crystallizes in the cubic space group $Pm\bar{3}m$, has been synthesized by mechanochemistry [16, 17]. Similarly, Watanabe *et al.* [18] showed that at high pressure syntheses, novel compositions of magnesium-copper system can appear, which may be potentially interesting for hydrogen storage applications. In this context, theoretical prediction of new structures, for instance of magnesium binary alloys, could support the experimental quest. With the substantial progress in computational science as well as in global structure search methods, it is nowadays possible to explore new crystalline phases using reliable calculations based on the electronic properties. In the present work, our aim is to investigate *in silico* the effect of pressure on $\text{Mg}X$ ($X = \text{Ba}, \text{Co}, \text{Cu}, \text{Ni}, \text{Ti}, \text{V}$) systems. Using an evolutionary algorithm (EA) in combination with first-principles optimization, to explore the compositional and configurational space, allows mapping the high-pressure phase diagram of Mg-based binary systems. Particular attention is paid to the compositions MgNi_3 and MgCu . For

these compounds, new hypothetical crystalline phases of hydrides were found. Detailed structures, as well as electronic and mechanical properties are presented and our results are promising and encourage the search for hydrogen storage alloys.

2. Computational details

2.1. Crystal structure prediction approach

For many years, the resolution of a crystal structure by theoretical means has been an almost insolvable problem. Recently, the rapid improvement of computational resources and methods has led to the appearance of many new methods for crystal structure prediction [19], which use physical phenomena (simulated annealing) or mathematical algorithms (Basin Hopping, Genetic Algorithm...). The widely used evolutionary algorithm (EA) belongs to one of the most effective methods and shows pertinent results [20, 21].

In the present work, the USPEX code developed by Oganov *et al.* [22, 23, 24], a prediction code based on the variable-composition evolutionary algorithm (VC-EA) was used for the prediction of crystal structures. Depending on the size of the system, unit cells containing 8-16 (for Mg–Ba, Mg–Co and Mg–Cu systems) or 12-25 (for Mg–Ni, Mg–Ti and Mg–V systems) atoms were considered. The calculations were performed both at 0 and 40 GPa external pressure. To ensure an unbiased and complete prediction, the following parametrization of the USPEX code was used: an initial population of 150 structures was generated randomly and afterward, 60 generations of 80 candidates were generated and considered. These 60 generations were obtained by applying variation operators on previous structures found, including heredity operations (*i.e.* combination of slices of two parents lattices), random production, and mutation operators (*i.e.* random exchange of different atoms, distortion of the crystal lattice, atomic displacements along the softest phonon mode eigenvectors). Finally, the additional inclusion of known crystal structures yielded an extra generation. Further and more detailed technical information on the USPEX evolutionary structural searches are given in the Supporting Information. Global searches for hydrides were carried out for the interesting alloys MgNi₃ and MgCu and consisted of an exploration of various hydride compositions with hydrogen ratios ranging from 1 to 5 atoms per unit cell. In order to relax the crystal structures at *ab initio* level using the density functional theory (DFT), calculations were carried out with the VASP package [25, 26, 27]. The energy calculations were based on the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parametrization [28].

Projected-augmented wave (PAW) potentials [29] were used, which had a [Ne] core (radius 2.0 u) for magnesium, [Ar] core (radius 2.3 u) for cobalt, copper, nickel, titanium, vanadium and [Pd] core (radius 2.8 u) for baryum. To improve the quality of the calculations, a multi-step relaxation of the structures was carried out using USPEX coupled with VASP. Once the final level of relaxation was reached, Monkhorst-Pack grid centered at the Γ -point with the resolution of $2\pi \times 0.05 \text{\AA}^{-1}$ to describe the Brillouin zone and a energy cut-off of 500.0 eV were used. Convergence criteria of 10^{-4} eV for the electronic properties and less than 1 meV \AA^{-1} for the ionic forces were applied. The Hellman-Feynman forces were minimized using a quasi-Newton algorithm. Such variable-composition calculations were executed both at 0 and 40 GPa external pressure.

2.2. Structure and electronic calculations

Once a set of candidate structures was identified (as discussed below), a more careful analysis was performed applying the criteria of 800.0 eV, 10^{-5} eV \AA^{-1} and 10^{-8} eV for the cut-off energy, the convergence of total energy and Hellmann–Feynman forces, respectively. Both spin and non-spin polarized calculations were performed for the structure that had been identified by the USPEX prediction calculations. The obtained energy difference were compared and since they were almost identical, a non-spin polarized state was assumed for all calculations. To obtain the accurate total energy as well as for the determination of the densities of states (DOS), the linear tetrahedron method with Blöchl corrections was used on the relaxed structures. In order to guarantee dynamic stability, phonon dispersion curves were calculated with the Phonopy code using density functional perturbation theory (DFPT) [30]. This allowed to apply the zero point energy (ZPE) correction for the calculation of formation energies. Additionally, the mechanical stability of the structures was examined based on the calculated elastic constants (bulk modulus B , shear modulus G and Poisson’s ratio ν) and using the stress-strain relations implemented in the VASP code. Furthermore, the charge distribution on the atoms was evaluated using Baders topological analysis [31]. Within this approach, the electron density is partitioned into regions linked by the minima of the charge density. Electronic density charge transfer and electron localization function (ELF) mapping as well as the 3D visualization of crystal structures were performed using the VESTA code [32].

The enthalpy of formation of magnesium based alloys Mg_xX_y is defined as follows:

$$\Delta H = E_{\text{el}}(\text{Mg}_x\text{X}_y) - xE_{\text{el}}(\text{Mg}) - yE_{\text{el}}(\text{X}) \quad (1)$$

where E_{el} denotes the calculated energy of various compounds. For hypothetical hydrides, the enthalpies of absorption are deduced from the equation :

$$\Delta H_{\text{abs}} = E_{\text{tot}}(\text{A}_m\text{H}_n) - mE_{\text{tot}}(\text{A}) - \frac{n}{2}E_{\text{tot}}(\text{H}_2) \quad (2)$$

where $E_{\text{tot}}(\text{A})$ represents the total energy of the theoretical and experimental structures MgNi_3 or MgCu and $E_{\text{tot}}(\text{H}_2)$, $E_{\text{tot}}(\text{A}_m\text{H}_n)$ are the total energies of the hydrogen molecule and the magnesium-based hydrides, respectively. These total energies include the contributions from the zero point energies (ZPE)[33] of compounds in the following way :

$$E_{\text{tot}}(\text{X}) = E_{\text{el}}(\text{X}) + E_{\text{ZPE}}(\text{X}) \quad (3)$$

The ZPE correction is of great importance for the correct calculation of hydride formation energies since the ZPE correction from hydrogen atoms in compounds present a substantial value and has a stabilizing effect, which is due to the low mass of hydrogen atom [34].

The energy of a H_2 molecule is approximated by DFT calculations using the molecule in a box approach, where hydrogen dimer was placed in a box with edges of $10 \text{ \AA} \times 11 \text{ \AA} \times 12 \text{ \AA}$ using Γ -point sampling. The results $E_{\text{ZPE}}(\text{H}_2) = 0.29 \text{ eV}$, $d_{\text{H-H}} = 0.757 \text{ \AA}$ and $E_{\text{binding}}(\text{H}_2) = 4.51 \text{ eV}$ are in good agreement with those reported in previous works [35, 36].

3. Results and discussions

Extensive structural searches on numerous magnesium-based binary alloys were carried at simulated pressures of 0 and 40 GPa. Since hydrogen storage for mobile applications, such as transportation, requires compounds with densities as low as possible, light elements of the first row Transition Metals (TM) have been studied, as well as an element of the alkaline earth metals for comparison. The goal of simulations at 40 GPa, a pressure that is difficult to reach experimentally, was rather to investigate if these systems were more favorable for alloys formation in a severe and drastic environment. These predictions could then give insight to scrutinize new alloys for systems sensitive to pressure. In this perspective, we investigate MgX ($X = \text{Ba, Co, Cu, Ni, Ti, V}$) systems and the results for transitions metals show that the pressure effect tends to stabilize new combinations with magnesium. At low pressure, a high number of $3d$ electrons of the transition metal seems to favor mixing with magnesium. Moreover, at high pressure, enthalpy

of formation of simulated Mg-TM alloys decreases further. In contrast, attempts with an alkaline earth metal, namely barium, shows a destabilization of the simulated alloys with increasing pressure, leading to a complete immiscible system where even the composition Mg_2Ba is unstable. Even though we have studied a number of Mg-TM systems in our work, we could not identify stable intermetallic phases for all of them. In the magnesium-titanium and magnesium-vanadium systems (see fig.S1 and S2), for example, no compounds were estimated as stable, even though at 40 GPa metastable intermetallics were found. In contrast, the magnesium-transition metal systems with cobalt, nickel and copper showed a radically different behavior with a wide range of new compositions at high pressure. Novel alloys, especially in the magnesium-rich area, are found and may serve as starting points for further experimental or theoretical examinations. We then focused on Mg–Ni and Mg–Cu systems in order to seek for positive effects of pressure on the stability of new phases and possible applications for hydrogen storage. It is worth noting that in spite of the extensive searches carried out in our study, we are not able to predict all the possible stable structures of the present systems. Since complex phases may be composed of more than thirty atoms in their primitive cell, and supposing that hydrides with high hydrogen ratio may exist, current predictions lack the necessary computational power to deal with phases that require high computational costs. High pressure new phases discussed here might be obtained experimentally using approaches such as high energy ball milling, and therefore in conditions far from equilibrium. It therefore should be noted that their utilization might be limited by the fact that upon cycling their re-formation might be hindered or not possible.

3.1. Structure prediction in the magnesium-nickel system

Fig.1 shows the enthalpy of formation of the generated structures in the magnesium-nickel system according to their composition. Without taking pressure into account, theoretical and experimental results are in perfect agreement: only the two well-known structures, the hexagonal phases Mg_2Ni and MgNi_2 with the space groups $P6_222$ and $P6_3/mmc$ respectively, are on the thermodynamic convex hull. This latter is a complete set of phases stable against transformation or decomposition into any other phases. Interestingly, we can note a metastable phase closest to stability with the MgNi_3 composition, which will be discussed later.

Under pressure of 40 GPa (fig.1), a broad variety of new compositions appeared to be stable, meaning that all structures are mechanically and dynamically stable according to calculations, even if some of them exhibit no particular geometry (see table 1). Only the hexagonal phase MgNi_2 remains identical to

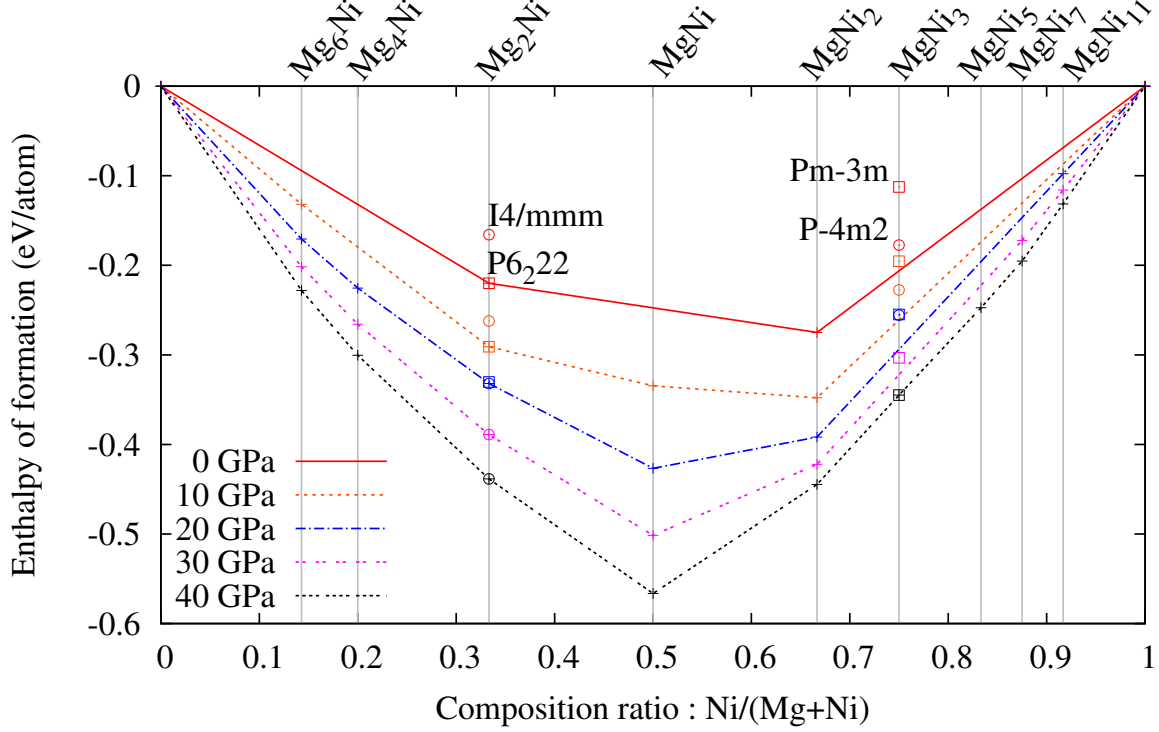


Figure 1: Stability of predicted structures in the Mg–Ni system with respect to pressure

the low pressure stable alloys.

As mentioned previously, stable phases could have a particular and complex structure, as it is the case for the metastable $\text{Mg}_{\sim 6}\text{Ni}$ [39] phase that have been experimentally identified as a Mg_6Pd -type structure containing more than a hundred atoms in its unit cell. Due to computational limits, one could not predict such an important structure in variable-composition studies. Nevertheless, a Mg_6Ni low symmetry phase has been found on the convex hull, demonstrating the efficiency of *ab initio* prediction for obtaining the right stable compositions, in default of the right structures. The composition MgNi_3 has also been synthesized experimentally under severe conditions [16, 17]. In the present study, depending on pressure, two competing phases for the ground state structure are found, a metastable phase at 0 GPa (with tetragonal structure, space group $P\bar{4}m2$) and a stable cubic phase at 40 GPa (space group $Pm\bar{3}m$, which is also found experimentally). The structural changes between the Ambient-(AP) and High-

Table 1: Calculated enthalpy of formation, structural and elastic parameters of stable and metastable phases in Mg–Ni system

| Structure and Space group | Lattice parameters | B (GPa) | G (GPa) | ν | ΔH (eV/atom) |
|--|---|------------|------------|-------|-------------------------|
| 0 GPa | | | | | |
| <i>Mg₂Ni</i> <i>P6₂22</i> (180) | $a = 5.20(5.205[37])\text{\AA}$ $c = 13.18(13.236[37])\text{\AA}$ | 65.47 | 30.80 | 0.297 | -0.20 |
| <i>MgNi₃</i> <i>P4₂m2</i> (115) | $a = 4.75\text{\AA} ; c = 6.74\text{\AA}$ | 136.7 | 67.92 | 0.287 | -0.17 |
| 40 GPa | | | | | |
| <i>Mg₆Ni</i> <i>P1</i> (2) | $a = 4.95\text{\AA} ; b = 4.96\text{\AA}$ $c = 7.76\text{\AA} ; \alpha = 80.1^\circ$ $\beta = 86.9^\circ ; \gamma = 84.8^\circ$ | 246.8 | 73.29 | 0.365 | -0.22 |
| <i>Mg₄Ni</i> <i>P2₁/m</i> (11) | $a = 4.93\text{\AA} ; b = 8.34\text{\AA}$ $c = 6.41\text{\AA} ; \beta = 101.2^\circ$ | 122.7 | 72.40 | 0.253 | -0.25 |
| <i>Mg₂Ni</i> <i>I4/mmm</i> (139) | $a = 2.87\text{\AA} ; c = 8.77\text{\AA}$ | 163.1 | 74.30 | 0.302 | -0.43 |
| <i>MgNi</i> <i>P4/mmm</i> (123) | $a = 2.72(2.99[38])\text{\AA}$ $c = 2.97(3.13[38])\text{\AA}$ | 204.5 | 103.3 | 0.284 | -0.56 |
| <i>MgNi₂</i> <i>P6₃/mmc</i> (194) | $a = 4.50(4.826[17])\text{\AA}$ $c = 14.78(15.832[17])\text{\AA}$ | 256.0 | 103.7 | 0.322 | -0.44 |
| <i>MgNi₃</i> <i>Pm3m</i> (221) | $a = 3.72(3.7163[17])\text{\AA}$ | 264.3 | 96.68 | 0.337 | -0.34 |
| <i>MgNi₅</i> <i>Cmmm</i> (65) | $a = 3.40\text{\AA} ; b = 10.24\text{\AA}$ $c = 3.38\text{\AA}$ | 280.8 | 115.6 | 0.319 | -0.25 |
| <i>MgNi₇</i> <i>Cmcm</i> (63) | $a = 4.78\text{\AA} ; b = 13.56\text{\AA}$ $c = 4.78\text{\AA}$ | 163.1 | 74.30 | 0.302 | -0.19 |
| <i>MgNi₁₁</i> <i>C2/m</i> (12) | $a = 8.25\text{\AA} ; b = 4.77\text{\AA}$ $c = 7.16\text{\AA} ; \beta = 125.1^\circ$ | 326.9 | 121.4 | 0.335 | -0.13 |

Pressure (HP) phases of MgNi_3 should be related by group-subgroup relations. The Bärnighausen tree is generally employed in order to illustrate these structural modifications [40, 41]. Using the symmetry group analysis [42, 43], there is no direct group-subgroup relation between AP and HP space groups. But there is a possible way using a hypothetical intermediate structure according to the following sequence : $Pm\bar{3}m$ (HP phase) $\longrightarrow P4/mmm \longrightarrow P\bar{4}m2$ (AP phase). This pathway seems perfectly consistent with the model prediction.

A careful theoretical examination of all possible phases was also carried out in the range of 0 - 40 GPa. With a step size of 10 GPa, a number of structures (ground state phases found by prediction and some interesting metastable phases) was completely relaxed to observe the convex hull aspect with respect to pressure (fig.1). Interestingly, from 10 GPa simulated pressure, one can observe the formation of the Mg_6Ni composition, in good agreement with the mild conditions of synthesis [39].

By mechanical alloying, Liu *et al.* found a new cubic phase MgNi_3 with the space group $Pm\bar{3}m$ and conclude that their process reached a pressure higher than 8 GPa, which is high enough for Mg to substitute Ni in its cubic phase with space group $Fm\bar{3}m$. The EA prediction performed at 40 GPa confirms this cubic phase of MgNi_3 as the global minimum energy structure. However, as mentioned previously, another structure, a tetragonal phase MgNi_3 with space group $P\bar{4}m2$, was predicted without pressure consideration. According to the low value of the energy of formation (see table 1), this tetragonal phase may be seen as a potential phase. The theoretical change of the ground state phase from the tetragonal to the cubic phase occurs between 20 and 30 GPa (see fig.1) whereas the cubic phase was experimentally formed at 8 GPa. This lead us to think, in agreement with Liu *et al.*, that kinetic effects aided by the grinding energy are governing this phase formation rather than pressure and thermodynamic. The formation of other Mg–Ni compositions seems to require drastic synthesis conditions, because a minimum pressure of 20 GPa is calculated. Moreover, the found Ni-rich alloys are not interesting in terms of light systems for hydrogen storage, and some of the structures found seem questionable given their low symmetry structure.

3.2. Structure prediction in the magnesium-copper system

The previous study has been repeated in the Mg–Cu system. From prediction at 40 GPa (fig.2), three new compositions in addition to known Mg_2Cu and MgCu_2 intermetallics, and an alternative structure for Mg_2Cu were found. For this system, all predicted structures exhibit reasonable geometry and are also determined to be stable (see table 2). Calculated values of the elastic moduli for MgCu and MgCu_2 in

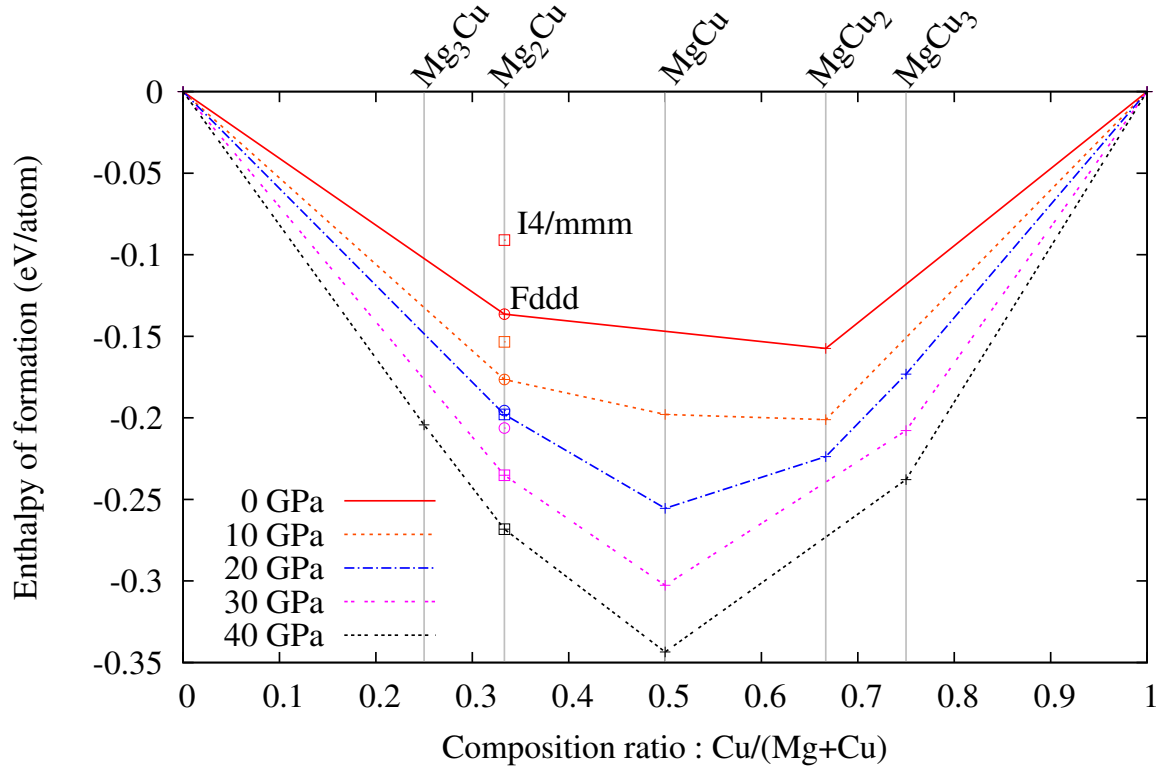


Figure 2: Stability of predicted structures in the Mg-Cu system with respect to pressure

table 2 differ from those reported in the references [44, 45]. These discrepancies are related to the high value of cut-off energy and k-points sampling we found necessary to obtain for a good convergence of elastic moduli (see Supporting Information section 3). Stabilities of Mg-Cu compositions are shown in fig.2 and the stabilizing effect of pressure on considered alloys can clearly be seen. It also indicates that significant pressure stresses is needed to obtain a spontaneous formation of these compounds.

We have not been further interested by the study of the hexagonal Mg-rich phase Mg_3Cu since it becomes stable only for high pressure superior to 30 GPa. However, it is interesting to note that Mg_3Cu hydride has already been synthesized [46] at 3.5 GPa and ~ 1100 K but the hydrogen free alloy was not observed. In contrast, the CsCl-type phase MgCu is the easiest affordable new composition and was experimentally discovered by Okada *et al.* under 6 GPa pressure at 1073 K [18]. Hydrogenation of this phase was not achieved but the authors assumed hydrogenation may be possible under suitable conditions.

Table 2: Calculated enthalpies of formation, structural and elastic parameters of stable and metastable phases in the Mg–Cu system at 40 GPa

| Structure and Space group | Lattice parameters | B (GPa) | G (GPa) | ν | ΔH (eV/atom) |
|-------------------------------|---|------------|------------|-------|-------------------------|
| Mg_3Cu $P6_3/mmc(194)$ | $a = 5.30\text{\AA} ; c = 4.25\text{\AA}$ | 152.1 | 50.12 | 0.352 | -0.197 |
| Mg_2Cu $I4/mmm(139)$ | $a = 2.95\text{\AA} ; c = 8.64\text{\AA}$ | 161.2 | 79.02 | 0.289 | -0.261 |
| $MgCu$ $Pm\bar{3}m(221)$ | $a = 2.85\text{\AA} ; a = 3.16\text{\AA}$ | 326.9 | 121.4 | 0.335 | -0.338 |
| $MgCu_2$ $Fd\bar{3}m(227)$ | $a = 6.49\text{\AA}$ | 220.4 | 84.89 | 0.329 | -0.237 |
| $MgCu_3$ $I4/mmm(139)$ | $a = 3.49\text{\AA} ; c = 7.03\text{\AA}$ | 228.8 | 79.56 | 0.344 | -0.233 |

According to them, the experimental temperature of 423 K during their hydrogenation attempt was likely too high for the hydride synthesis, meaning that an interesting low stability hydride might exist. This hypothesis is in excellent agreement with our present results shown in the next section. Furthermore, the calculated stability of the MgCu compound suggests that a direct and lower temperature synthesis is possible if the pressure conditions are set to approximately 10 GPa. At such pressure, hydrogenation at low temperature could be likely achieved. Okada *et al.* have also synthesized a novel compound $Mg_{\sim 51}Cu_{\sim 20}$ similar to the $Mg_{51}Zn_{20}$ phase with space group $Immm$. This structure with numerous atoms in the primitive cell is out of range of our proof of principle calculations. However its composition ratio $Cu/(Mg + Cu)$ of 0.28 is closed to the 0.25 of the Mg_3Cu predicted crystal and demonstrates that genetic algorithm method are a efficient tool to predict possible mixed compounds.

3.3. The hypothetical hydrides of $MgNi_3$ and $MgCu$

As mentioned previously, the novel compounds $MgNi_3$ and $MgCu$ have been synthesized recently and particular attention has been paid to these compositions in the present study in order to shed more light on possible hydrogenation. The electronic structure calculations show that the two alloys exhibit a metallic character as can be seen in the total and partial electronic densities of states (DOS and PDOS)

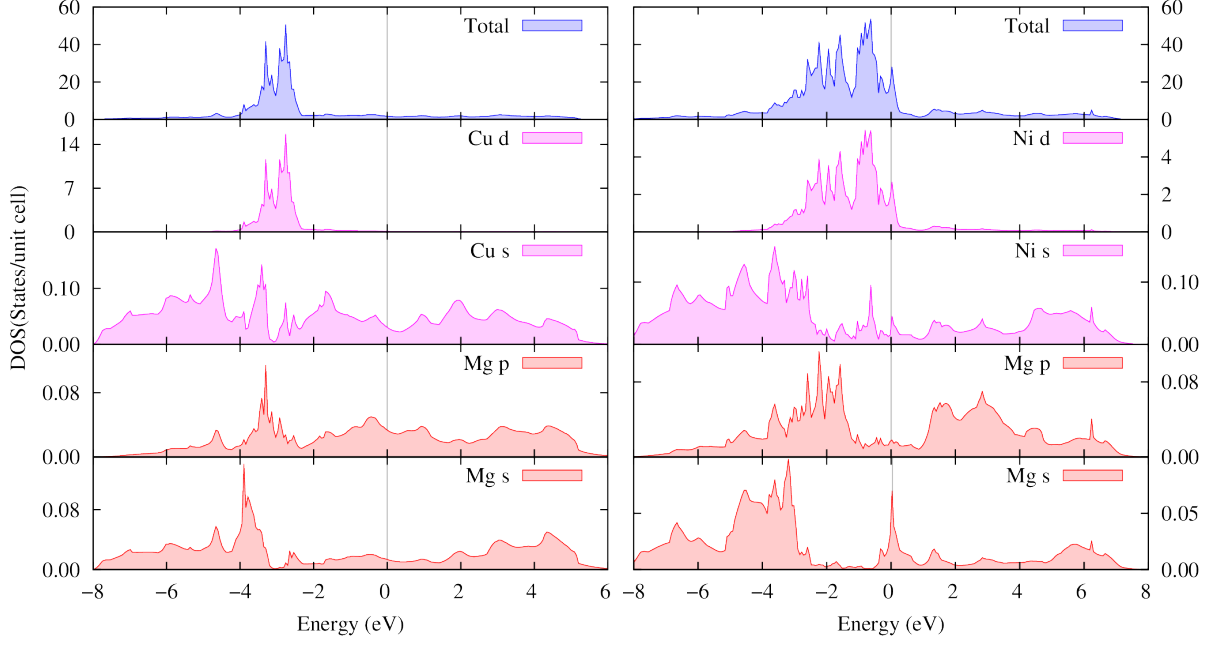


Figure 3: Total and partial density of states of MgCu (left) and MgNi₃ (right).

(fig. 3). Due to the low electronegativity of magnesium compared to copper and nickel, Mg acts as a partial electron donor. This observation is confirmed by the Bader charge analysis, which yields a $0.20e$ and $0.89e$ electron transfer from Mg to Ni and Cu, respectively. In Ni-based alloy, the excess electron on Ni is located in the d -band and the Fermi surface lies in the highest metal d -states. In MgCu, the d -states of Cu are filled so that the Fermi level lies beyond them. The magnesium-metal atom distance is smaller for MgNi₃ ($d_{\text{Mg-Ni}} = 2.58 \text{ \AA}$ compared to $d_{\text{Mg-Cu}} = 2.74 \text{ \AA}$ for MgCu). In spite of a shorter distance, the ionic bond for MgNi₃, denoted by the charge transfer between atoms, is very weak and one could then expect an easier distortion of the lattice for the latter compound.

To ensure totally unbiased searches of hydrides, no starting geometry was given or recommended to the genetic algorithm. More than six thousand different structures were generated and among the most stable hydrides predicted, two were kept for further investigations since they exhibit high symmetry structures (see table 3), namely MgNi₃H₂ and MgCuH₃ with a trigonal structure.

To explore hydrogenation, one usually considers the process as presented into different contributions [47, 48] : conversion of the crystal, expansion of the structure and hydrogen insertion ; the first two being

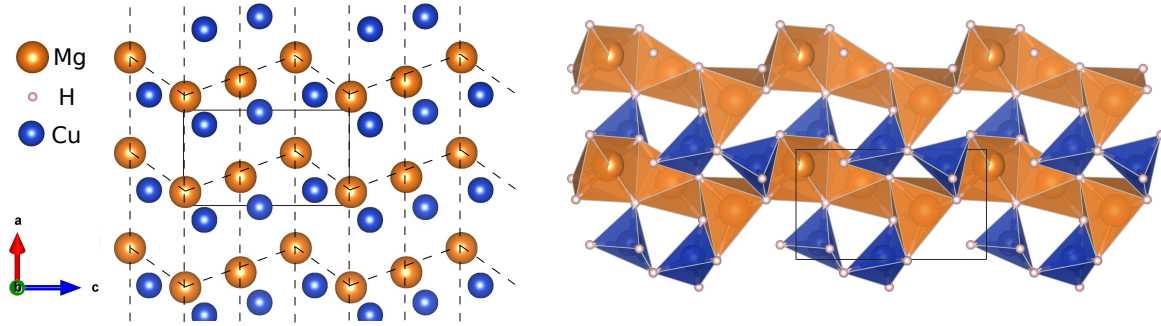


Figure 4: Left : Relationship of the hydrogen free crystal structure of MgCuH₃ to a cubic closest packing. Trigonal unit cell is indicated by solid lines, pseudo-cubic cells by dashed lines. Right : Structure of MgCuH₃, as seen as a stack of Mg hydride pyramid and Cu hydride tetrahedron.

destabilizing steps compared to the third. Particularly, the conversion step is really energy demanding when alloy and hydride have a rather different crystal structure, as, for instances, shown in our previous work on the arsenic-palladium system [34].

Interestingly, a simple *ab initio* relaxation of hydride structures with hydrogen atoms removed leads directly to the ground state structure of MgNi₃ and MgCu, meaning that structures of hydride and hydrogen hosts are very close to each other in the energy landscape. For MgNi₃ and its hydride (fig.7), this point was confirmed with further calculations and is in agreement with the work of Miwa and Fukumoto [47] who showed that the lattice expansion is a dominant factor for *d*-metals around the 8th column. The hydride structure can be considered as a distorted Cs–Cl structure. In contrast, it is somewhat surprising to see how easily MgCuH₃ hydride structure relaxes to Cs–Cl ground state symmetry. Nevertheless, the compound crystallizes in the strongly distorted cubic closest packing, as can be seen on fig.4.

The calculated absorption enthalpies of the studied hydrides (table 3) are singularly different regarding the fact that both hydrides and alloys have the same structure type. It is worth noting that neglecting the ZPE correction would lead to incorrect enthalpies, especially for MgCuH₃ hydride where its omission leads to a non-spontaneous formation. Furthermore, one could expect the hydrogen richest compound MgCuH₃ to be the most stable since hydrogen has generally a stabilizing effect. To explain the difference, a precise study on electronic structures was carried out, especially using electron localization function (ELF) and electron charge density transfer. In ELF, electrons localization information is given by the probability for finding a second like-spin electron near a reference point. It allows to view the system in more chemical aspects, particularly different bonding interactions. The charge density transfer is an

Table 3: Enthalpy of absorption, structural and elastic parameters of predicted hydrides

| Structure and Space group | Lattice parameters | B (GPa) | G (GPa) | ν | $\Delta H(\text{eV/atom})/(\text{kJ mol}^{-1} \cdot H_2)$ |
|--|--|------------|------------|-------|---|
| <i>MgNi₃H₂</i> <i>P3₁21(152)</i> | <i>a</i> = 5.30 Å <i>c</i> = 6.47 Å | 31.83 | 24.96 | 0.189 | -0.134 / -77.7 |
| <i>MgCuH₃</i> <i>P3₂(145)</i> | <i>a</i> = 4.92 Å <i>c</i> = 7.41 Å | 139.3 | 71.93 | 0.280 | -0.00971 / -0.312 |

efficient way to visualize changes in electron density upon hydrogen insertion into alloys. It is obtained by calculating the difference in charge density between the hydride and the same hydride structure with hydrogen atoms removed.

Overall, the stabilization of both hydrides is confirmed by the strong electron gain (transfer) and electron localization around the hydrogen sites (fig.6). The densities of states (fig.5) also demonstrate that the stabilization occurs by interaction of metals states with hydrogen *s*-states in wide energy range below the Fermi level, causing delocalization of metal states in the low-energy region. A medium loss of the *d*-orbital occupation of the transition metals is seen in the electron charge density in the direction pointing towards the hydrogen atoms, which arises from the formation of a bonding-antibonding pair between the directly overlapping H *s* and Ni or Cu *e_g* orbitals. Nevertheless, the electron density change on transition metals is weak, because the *d*-states are filled or almost filled. The Bader charge analysis also confirms the hydridic behavior by the negative charge of the hydrogen atoms, and the values of $-0.58 e$ for MgCuH₃ and $-0.85 e$ for MgNi₃H₂ are consistent with the electronegativity of metals and results reported in other works [49, 50]. In addition, the Bader analysis indicates that electron transfer originates mainly from Mg atoms (Mg net charges are respectively $1.59 e$ and $0.80 e$ for MgCu and MgNi₃ hydrides) and that a large transfer for MgCuH₃ may be a reason for the large structure distortion.

In MgCuH₃, five H atoms form a deformed square-based pyramid around the Mg atoms and Cu atoms are surrounded by four hydrogen atoms in a distorted tetrahedral environment, with the resulting polyhedra constituting of puckered sheets. Thus, the hydrogen atoms interact with copper as well as with magnesium, which leads to an overlap between hydrogen and metals orbitals, as indicated by the PDOS. The electronic structure shows a non-metallic character with a band gap of 2 eV. Compared to the DOS of the MgCu alloy, one can see clearly that this band gap results from the displacement of Mg-states to lower energy levels due to Mg-H interactions, and the down-shift of the Fermi level to the top of the copper *d*-band. The overall DOS appearance is comparable to the DOS found for the intermediate, but

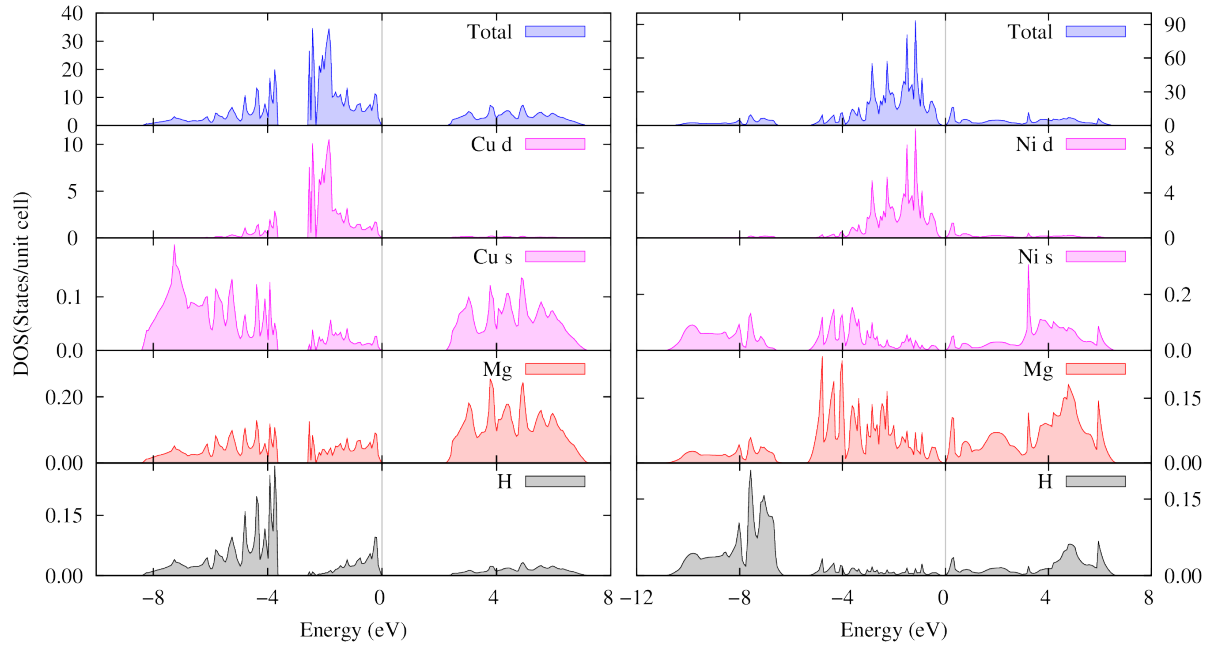


Figure 5: Total and partial density of states of MgCuH₃ (left) and MgNi₃H₂ (right).

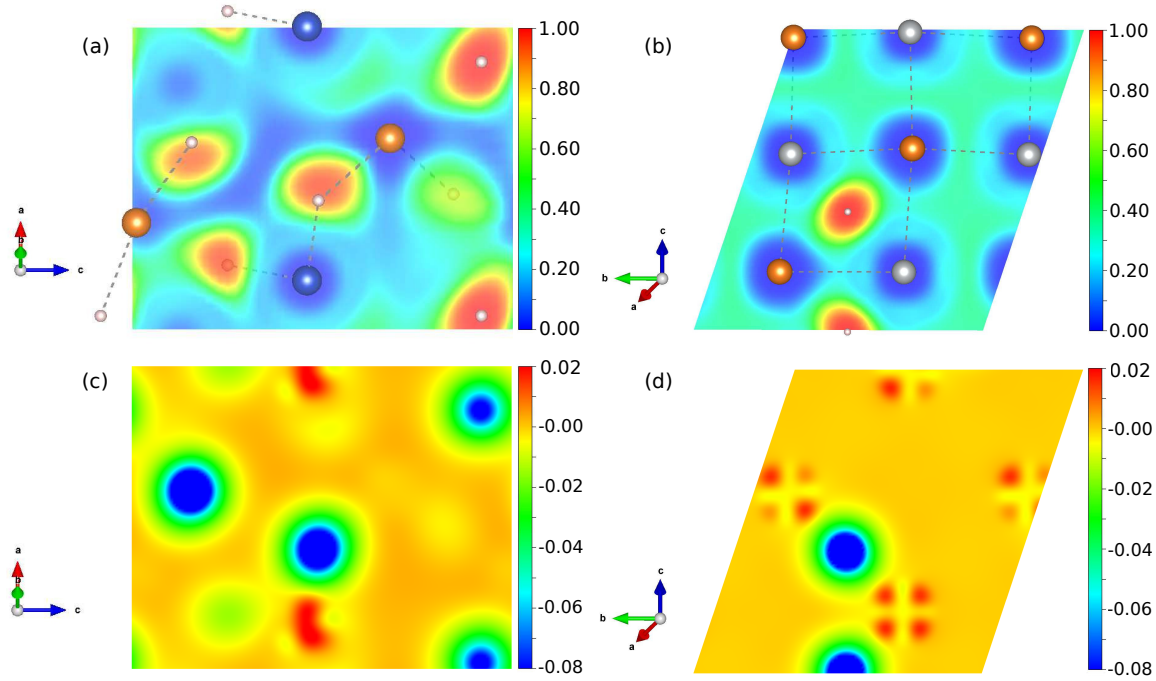


Figure 6: Electron localization function (ELF) (a,b) isosurface and electron charge density transfert (c,d) on (010) plane for MgCuH₃ (left), on (101) for MgNi₃H₂ (right).

not the late 3d transition metal hydrides as described in the detailed study of Smithson *et al.* [48]. Here, the destabilizing effect of hydrogen atoms on copper is counteracted by the partial substitution of Cu by Mg in the structure.

Moreover, the average ELF value between Mg or Cu and H is less than 0.3, which suggests the absence covalent bonding but the presence of ionic bonds. The latter is confirmed by the difference in the charge density and Bader charge analysis, as described previously.

In the MgNi₃H₂ structure, hydrogen atoms are partially filling octahedral sites of the distorted Cs–Cl structure (fig.7). The PDOS shows a dominant interaction of hydrogen with magnesium at a new low-energy region, which leads, apart from this new region, to a similar DOS as the hydrogen-free MgNi₃. The hydride then keeps a metallic character. The main interaction between Mg and H is also indicated by the ELF where electron localization around hydrogen are pointing preferentially towards Mg atoms. The large region where the ELF value is 0.5 in volume separating atoms clearly corresponds to an electron-gas-like pair probability, as expected within a metallic network. Finally, the significant 0.85 *e* charge transfer to H

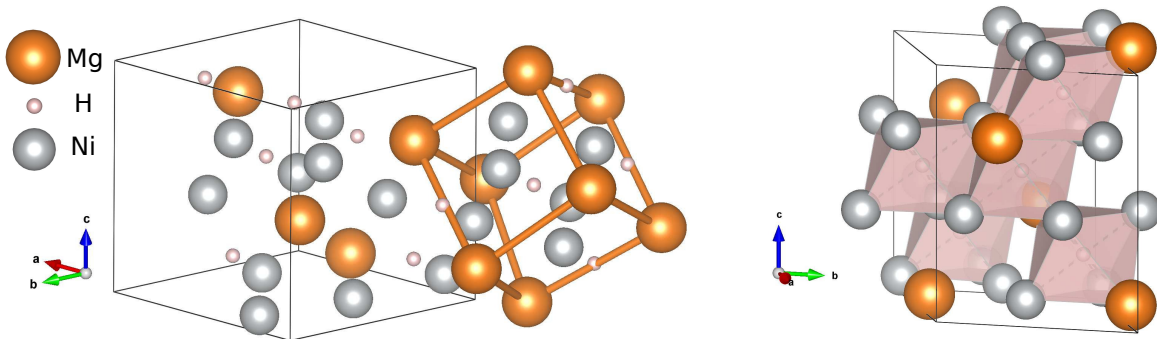


Figure 7: Left : Trigonal unit cell of MgNi_3H_2 (in solid lines) and its distorted Cs-Cl type structure (in orange lines). Right : Representation of octahedra sites containing hydrogen atoms.

and the weak contribution of structure conversion and lattice expansion steps complete the explanation of the difference of the enthalpy of absorption of the two considered hydrides. It is nonetheless important to emphasize that the enthalpy of formation of MgNi_3H_2 is of the same magnitude as MgH_2 hydride. More generally, the calculated enthalpies for both studied hydrides make these last very interesting for hydrogen storage applications.

4. Conclusions

We have performed a systematic study on the phases stability of the binary alloys of magnesium and a number of $3d$ -transition metals systems at ambient and high pressure, using the USPEX code with *ab initio* calculations. Novel structures were predicted for the systems Mg-Ni and Mg-Cu and the calculations indicate that the new predicted phases are dynamically and mechanically stable. Moreover, our investigation points out the existence of possible hydrides of MgNi_3 and MgCu . The results obtained are in agreement with the electronic study concerning their structure and relative stability. As expected, there is a stronger hybridization between hydrogen and magnesium atoms than hydrogen and transition metals. For the considered systems, hydrogen interactions have stabilizing effects. The presence of magnesium plays a crucial role on the stability of the hydride of MgCu . The impact is lower in MgNi_3 since the $\text{Ni} - 3d$ states are not completely filled. The fundamental destabilizing factor in hydride formation remains the phase change and this step can be tailored by alloying different elements to form an appropriate host for hydrogen. In this context, finding the ground-state of hydride is an important point and genetic algorithms represent an efficient approach.

Besides the limitations of evolutionary algorithms for structure investigations such as crystals with large unit cells or amorphous phases, it can be clearly seen that this approach is a powerful tool to screen the composition variations of binary alloys, as shown in the present study with respect to pressure modifications. At least, a stable composition range can be highlighted and give useful insights and trends as shown for the predicted Mg_6Ni and Mg_3Cu alloys. The found theoretical hydrides seem to reflect experimental expectations. That is the reason why the genetic algorithm approach should belong to every rigorous structural study since it allows tailoring exotic and non conventional structures, which are common, especially in compounds composed of highly heterogeneous atom combinations.

Results and outlooks presented here are encouraging and motivate for further studies on the design of hydrogen storage alloys.

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