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Hydrogen storage in Mg*X* (*X* = Cu and Ni) systems - is there still news?

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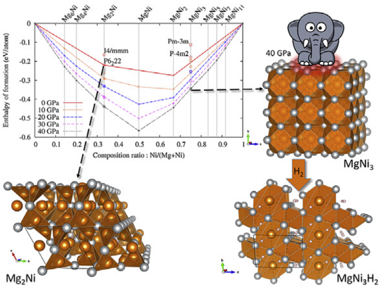
HIGHLIGHTS

- Phase diagrams of Mg-Ni (-Cu) binary are studied by Evolutionary Algorithm and DFT.
- Pressure change the minimum energy compositions and new structures are predicted.
- MgNi3H2 and MgCuH3 seems to be very interesting for hydrogen storage applications.

GRAPHICAL ABSTRACT



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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 reveals 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 encourages the use of similar prediction schemes in order to identify and design destabilized systems for hydrogen storage applications.

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. 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

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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 [9–12]. 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 MgX (X = Ba, Co, Cu, Ni, Ti, 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. [22–24], 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 if 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 $MgNi_3$ 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 [25–27]. 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 $2\pi \times 0.05$ $Å^{-1}$ 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 1meV$Å^{-1}$ 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^{-3} eV$Å^{-1}$ 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 3*D* 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:

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

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

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

where $E_{\mathrm{tot}}(\mathrm{A})$ represents the total energy of the theoretical and experimental structures $MgNi_3$ or MgCu and $E_{\mathrm{tot}}(\mathrm{H}_2)$, $E_{\mathrm{tot}}(\mathrm{A}_m\mathrm{H}_n)$ 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: