

Materials for hydrogen storage

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ABSTRACT
In the present article two systems studied theoretically in the Physics Department of the Universidad Nacional del Sur are presented. Both are related to the Physics of Materials, more specifically to intermetallic hydrogen storage materials, and have been developed using self-consistent Density Functional Theory (DFT) calculations. DFT is a phenomenally successful approach to finding solutions to the fundamental expression that describes the quantum behaviour of atoms and molecules, the Schrödinger equation, in settings of practical value.

Laves phases, under the representative forms cubic MgCu_2 (C15) and hexagonal MgZn_2 (C14) and MgNi_2 (C36), have been extensively studied due to their promising behavior as solid state hydrogen storage materials, ease of synthesis by the conventional cast methods, flexibility in tailoring the thermodynamic properties and good absorption/desorption kinetics and cycle life. However, they cannot be used for technological applications because of its too strong hydride stability at room temperature.

In this work we studied the hydrogen absorption for $\text{Zr}(\text{Cr}_{0.5}\text{Ni}_{0.5})_2$, isostructural with the MgZn_2 Laves phase, with the aim to find the most energetically favorable interstitial sites to locate hydrogen. Bulk modulus and volume cell changes due to the hydrogenation process were also analyzed for this phase.

According to literature, the most stable were the A_2B_2 sites, with an absorption energy average of -0.25 eV, followed by the AB_3 sites. Bulk Modulus fluctuated in the range of 150 and 165 GPa.

Key words: Laves phases, hydrogen absorption, DFT.

INTRODUCTION

Need of new energies

For decades, the aim to find an appropriate solution to the current energy sector has been a challenge, and it still remains so. The need to reduce or eliminate the historical dependence on fossil fuels, as well as to stop harmful emissions that causes the greenhouse phenomenon with its obvious climate change, is evident. In addition, fossil fuel-based energies are also subject of a strong economic and geopolitical discussion.

It is worth highlighting that even though carbon dioxide emissions are the main reason of the greenhouse effect, the uncontrolled combustion of fuels derived from coal, combined with deforestation, transfer more CO_2 into the atmosphere than it is possible to remove naturally through carbon sedimentation. This problem causes a notable gas concentration increase in a short period of time and dismisses the contribution of the own natural carbon cycle.

In all aspects, the world calls for sustainable carbon-free energy technologies. It is a fact that sooner or later fuel resources will be gone, but behind this apparently tragic conclusion many alternative energies sources appear to support all demands. One possible technical way to overcome these issues is the hydrogen-based economy.

In daily life, in a wrong or inadvertent way, people use to refer to hydrogen as an energy source or a primary energy properly speaking. Never-

theless, it is an energy vector, the most promising energy carrier that could store great amounts of energy that then could be released for using with productive purposes.

On the other hand, hydrogen can be obtained from water, process that would not generate toxic or dangerous waste if the resources provided come from clean sources. Its combustion with pure oxygen, that only produces water, closes an ideal cycle for a sustainable development in time. That is why it is also consider an infinite energy.

Hydrogen is abundant and a non polluting material. Since carbon is not involved in combustion, no CO_2 is produced while combustion is taking place and no climatic effect is enhanced.

For this reasons, hydrogen seems to be a possible future solution. It is a good time to review the science and the engineering of hydrogen storage technologies.

But, why hydrogen?

Because it has the highest specific energy (energy/mass) for being the lightest element in nature. This means that, in comparison with the rest of the substances, the energy per unit mass that hydrogen releases is much larger than carbon, methane, natural gas or gasoline (Table I).

At the same time, it has the lowest ratio between energy and volume (energy/volume) owing to the fact that its density as diatomic gas in normal conditions of pressure and temperature (100 KPa, 273 K) is $\rho_{\text{H}_2, (\text{NTP})} = 0,0898 \text{ kg/m}^3$. This is the same to say that 1 kg of hydrogen in normal working conditions occupies 11.135 m^3 .

Clearly, if this value is compared to methane, the main component of natural gas (which density is $\rho_{\text{CH}_4, (\text{NTP})} = 0.7167 \text{ kg/m}^3$ and implies that 1 kg_{CH_4} occupies 1.40 m^3), the disadvantage is remarkable.

However, although methane may fill a volume about eight times lower, its energy is also three times lower with the additional consequence that its burning emits CO_2 .

Table I - Specific energy of several fuels

	Fuel	Specific Energy (MJ/kg)
Gas (NPT)	Hydrogen	120
	Methane	41
	Natural Gas	38 - 47.16
	Ethane	52
	Propane	46
	Butane	46
Liquids	Gasoline	43
	Benzene	42
	Ethane	30
	Methane	20
	Ammonia	21
Solids	Carbon	31
	Wood	17

So, despite density is the main inconvenience to store and transport hydrogen, one of the simplest methods is to use it as compressed gas. Here, hy-

drogen can reach densities of about 36 kg/m^3 at the expense of consumption of big quantities of energy and the risk of working with high pressures (20,000 - 80,000 KPa).

Liquid form is another alternative but requires cryogenic temperatures (20.15 K) at normal pressure. In these terms, beside the energy needed to create such extreme conditions, heat transfer through the walls of the storage devices causes hydrogen losses by evaporation and consequently atomic diffusion. Therefore, these applications are reserved for industrial activities

Metal hydrides are also an option. They are chemical compounds that can absorb and desorb hydrogen at room temperature and constant pressure, close to atmospheric pressure.

Then, carbon nanotubes, activated carbon, clathrates and certain molecule metal body arrangements, named as porous structures, are other techniques in researching process.

Finally, intermetallic compounds, like reversible AB_n alloys, are also considered for hydrogen-storage applications. Particularly, the AB_2 or Laves phases [1], have been extensively studied due to their reasonable hydrogen storage capacity, ease of synthesis by the conventional cast methods, flexibility in tailoring the thermodynamic properties and good absorption/desorption kinetics and cy-

cle life. In these kind of materials, atomic hydrogen is forced to diffuse into the bulk, bind to host elements in specific sites in the crystal structure and then forced again to leave the main matrix. Ideally, these materials would absorb and release hydrogen in and out of their interstitial sites with little energy requirements.

Hydrogen effects on the chemical bonding, electronic structure and mechanical properties within Laves phases have been studied by many authors, both experimental and theoretically.

In the computational simulation field, van Mid-den et al. [2], for instance, studied the structural and electronic properties of the hydrogenated $ZrCr_2$ C14 Laves phase adding one or two hydrogen atoms per primitive cell and tested seven possible independent tetrahedral interstices for hydrogen absorption. Besides this report, Gesari et al. [3] also analyzed the hydrogen absorption in $Zr_{0.9}Ti_{0.1}NiMn_{0.5}Cr_{0.25}V_{0.25}$ C14 alloy and calculated the binding energy for hydrogen in different tetrahedral sites with a variety of local environments.

Matar also reported a detailed review of inter-metallic hydrides considering the contributions of ab-initio calculations to the understanding of chemical bonding and magnetism in binary and ternary Laves phases.

On the other hand, in an experimental study, Yongquan et al. [4] studied the electrochemical performances of $Zr(Cr_xNi_{1-x})_2$ ($0.15 \leq x \leq 0.65$) alloy with the goal of knowing how different Cr concentrations modify the hydrogen storage capacity of the material. They also report the sites where hydrogen is absorbed.

To the best of knowledge, there is no detailed experimental data available in the describing the hydrogen location in a Zr-Cr-Ni Laves phase.

In this article, we report a theoretical effort to find the most energetically favorable locations of interstitial H atoms in the C14 $Zr(Cr_{0.5}Ni_{0.5})_2$ host unit cell. The Bulk modulus is also described with the help of the Birch-Murnaghan [5] equation of state.

CRYSTAL STRUCTURE

Laves Phases

Three crystal structures, known as Friauf-Laves phases or more commonly Laves phases, have been observed to associate with the ideal stoichiometric AB_2 -type intermetallic compounds: cubic $MgCu_2$ (C15) and hexagonal $MgZn_2$ (C14)

and -less frequently- $MgNi_2$ (C36) [6-10] (Figure 1, Table 2). A atoms are usually transitional metals, like zirconium or titanium, while B can be chromium, nickel or vanadium, among other metallic elements.

Laves phases are classified purely based on the geometry of the crystals, being indifferent the chemistry nature of the metallic atoms or the number of its valence electrons and meaning that the exclusive geometry factor is the atomic size ratio between both components, expressed as the ratio of the atomic radii of the two neutral atoms A and B: $r_A/r_B \approx \sqrt{3}/\sqrt{2} \approx 1.225$ (with a range of 1.05-1.68) [11]. When this condition is satisfied, groups of packed spheres can occupy the space in a particularly striking mode. In these structures, both A and B atoms are related in the crystal lattice in such a way that the distance between the nearest A and B atoms in the metal is greater than the mean distance between the nearest A or B atoms. Then, if both lattices are interpenetrated not much space is empty and each of A and B atoms remain surrounded by 12 and 6 neighbours, respectively (Figure 2).

Representing the best space filling arrangement possible for unlike spheres, Laves phases are also an example of tetrahedrally close-packed or t.c.p. structures [12], since all of their interstices are formed by tetrahedra of variable regularity, in contrast to the traditional close-packed structures adopted by monatomic solids and alloys with atoms of approximately equal size, where both tetrahedral and octahedral interstices can be differentiated.

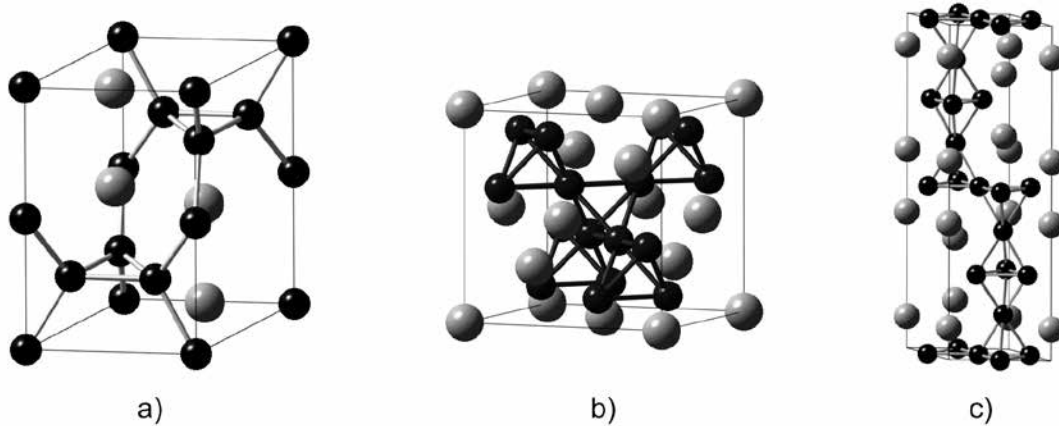


Figure 1 - Schematics of the three Laves phases in their AB_2 -type representative forms: a) $MgZn_2$ (C14); b) $MgCu_2$ (C15); c) $MgNi_2$ (C36). They can also be presented with other substitutes elements.

Table 2 - Laves phases unit cell parameters.

	$MgZn_2$ (C14)	$MgCu_2$ (C15)	$MgNi_2$ (C36)
a (Å)	5.221	7.048	4.815
b (Å)	5.221	7.048	4.815
c (Å)	8.567	7.048	15.8
α	90°	90°	90°
β	90°	90°	90°
γ	120°	90°	120°

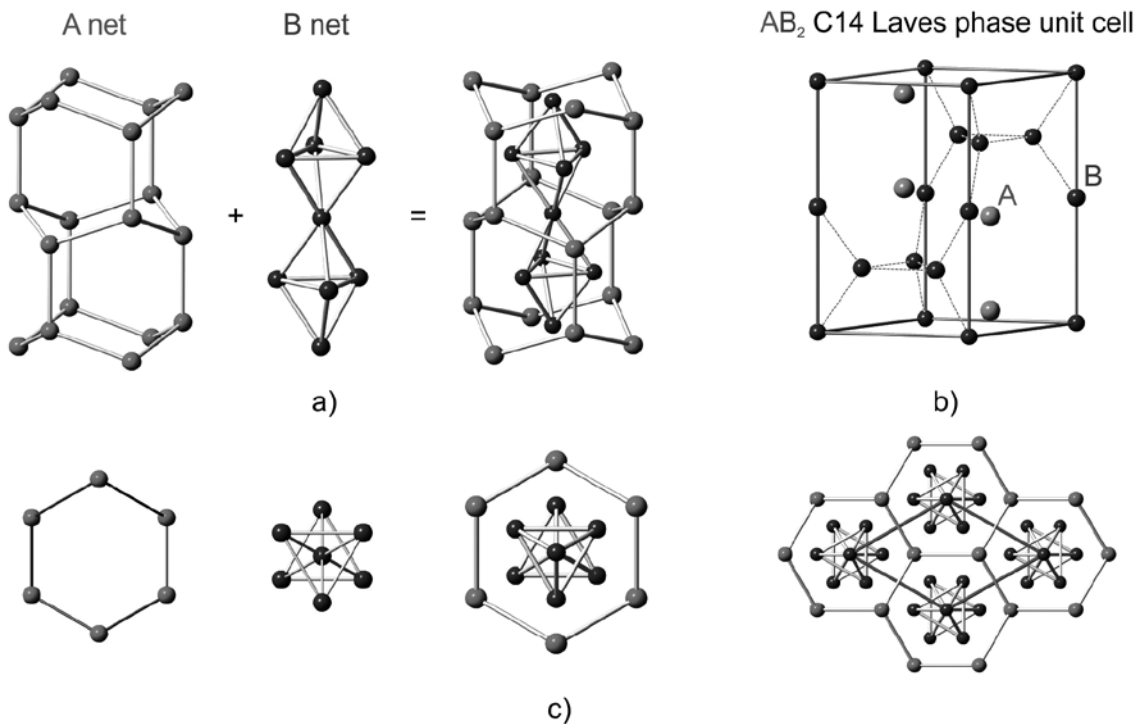


Figure 2 - a) A and B nets merged to form a C14 Laves phase; b) C14 unit cell; c) Top views of all perspectives.

For all mentioned, and due to the fact that these interstices present a suitable binding energy for hydrogen which allows its absorption or desorption near room temperature and atmospheric pressure, these phases have revealed a promising behaviour as solid state hydrogen storage materials [13-15].

Three distinct types of tetrahedral sites available for storing hydrogen can be identified in C14

structures: 12 A_2B_2 sites per A atom, 4 AB_3 sites and 1 B_4 site per formula unit (Figure 3). A total of 17 tetrahedrally coordinated interstices per AB_2 formula that may hold a considerable amount of hydrogen. Considering the seven possible independent hydrogen positions per unit cell and multiplying them by their symmetry, there are 68 possible sites where the H atoms could be located, resulting in $A_4B_8H_{68}$ (Figure 4)

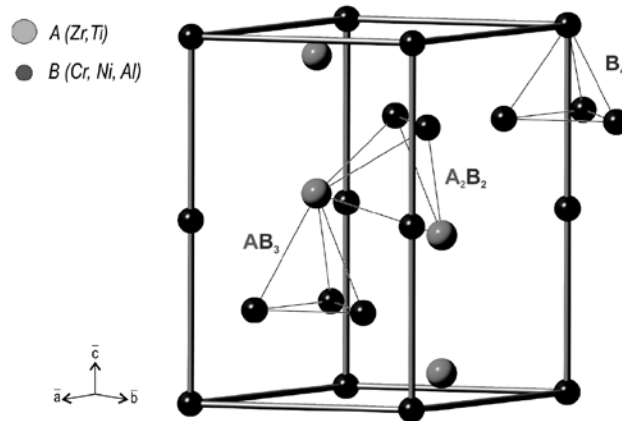


Figure 3 - Unit cell of the hexagonal C14 Laves phase with the three types of tetrahedral interstices that are present: A_2B_2 , AB_3 and B_4

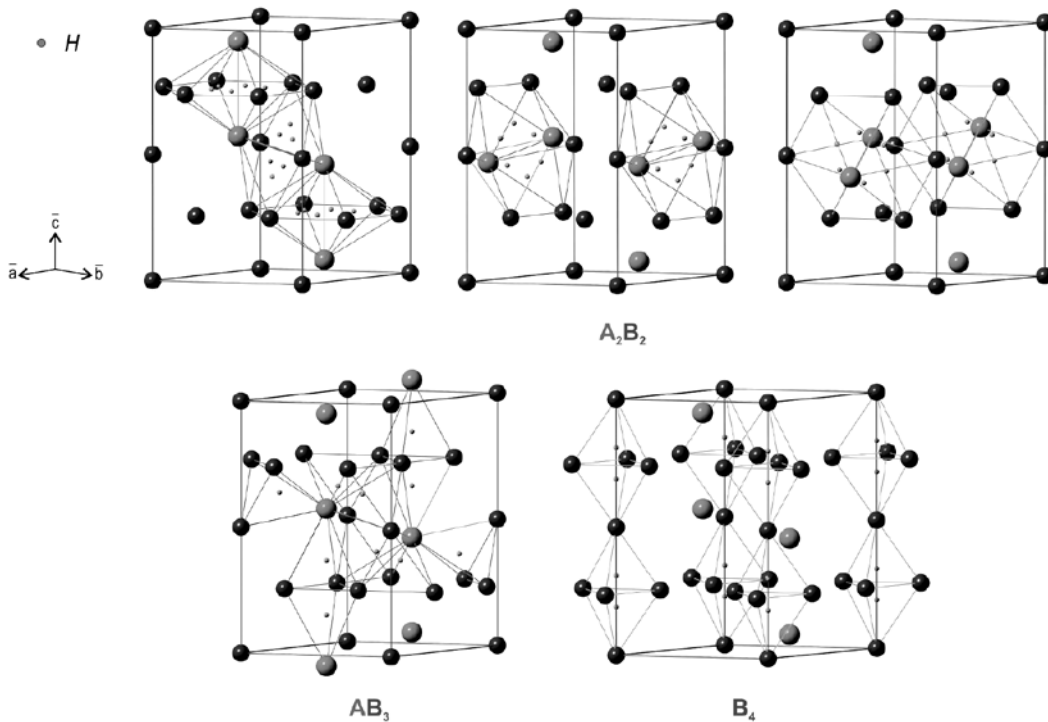


Figure 4 - All possible sites to locate H. Adding the four A-atom neighbours outside the hexagonal faces and other A and B atoms from the net, there are 24 A_2B_2 tetrahedra that has the central A atom as one apex (and that, by symmetry, turn into a total of 42 A_2B_2 sites), 10 AB_3 sites and 16 B_4 distorted icosahedra sites. Hydrogen atoms are represented by small light blue spheres.

Many works probed that compositional substitutions of metallic elements in Zr-based AB_2 Laves crystals, such as $ZrMn_2$, $ZrCr_2$ and ZrV_2 , isos-structurals with the hexagonal Laves phase $MgZn_2$, could intensify the hydrogen absorbing/desorbing kinetics and electromechanical capacity of these compounds. However, despite the important hydrogen capacity of these phases, they are not suitable for technological applications since its strong hydride stability. Previous studies reported that the partial substitutions of Cr by other transition metal, like Ni, could destabilize the hydride [16].

In special, the intermetallic $ZrCr_2$ can be either C14 or C15 phase depending on the synthesis conditions. According to documents, if 10% if 50% of Cr is replaced by Ni, resulting in $Zr(Cr_{0.5}Ni_{0.5})_2$, it becomes a C14 $MgZn_2$ -type structure [17].

COMPUTATIONAL METHOD

Simulations were carried out with the Vienna Ab initio Simulation Package (VASP), which is based on DFT [18].

As it is not possible to resolve analytically the Schrödinger equation for systems with more than three interacting particles, VASP uses certain approximations that have to do with the resolution of Kohn and Sham (K-S) equations.

It works with plane waves and ultrasoft potentials. Plane waves are used to expand the K-S electronic wave functions and pseudopotentials are used to assign an average value to the potential in the zone where electrons are much closer to the nucleus.

Besides, to apply the K-S equations is necessary to know very well the interchange and correlation functional form. Because this is not feasible in an accurate way, some other approaches have been developed to represent the terms.

So, in this study, potentials within the projector-augmented wave method (PAW) and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE) were used [19].

Lattice parameters were determined by minimizing the total energy of the cell with a conjugated-gradient algorithm to relax ions. The Brillouin-zone integrals were approximated using a $7 \times 7 \times 7$ mesh centered on Γ -point (Gamma-point). All calculations were performed with an energy cut-off of 450 eV for the plane wave basis set.

Hydrogen absorption energy was defined as following:

$$E_{\text{ABS}} = [E(\text{AB}_2\text{H}) - E(\text{AB}_2) - n/2 \cdot E \text{H}_{2(\text{g})}] \cdot 1/n \quad (1)$$

The first term on the right-hand side is the total energy of the AB_2 cell with one hydrogen atom; the second term is the total energy of the pure intermetallic and the last term is the H atom or the half hydrogen molecule total energy. The first two terms are calculated with the same relaxation parameters and the last one is found by placing a H_2 molecule in a 10 \AA side cubic box and carrying out a Γ -point computation.

With this definition, negative absorption energy values correspond to a stable configuration.

RESULTS

Lattice parameters were calculated after geometry optimization of the alloy structure without H. The computed lattice constants are $a = 5.022 \text{ \AA}$ and $c = 8.241 \text{ \AA}$ (Table 3). Unfortunately there is no experimental data for a direct comparison, more than $ZrCr_2$.

Table 3 - Lattice Parameters for $Zr(Cr_{0.5}Ni_{0.5})_2$

	Experimental (*)	Calculated
a (Å)	5.221	5.022
c (Å)	8.567	8.241
c/a	1.64	1.64
(*) For $ZrCr_2$		

To find the hydrogen absorption sites, we first considered the system containing only one H atom in the cell. We carried out total energy calculations for the H atom located at the three different interstitial sites mentioned before, each with a different environment, finding that the lowest energies were mostly located in the A_2B_2 interstitial sites, followed by the AB_3 sites. B_4 sites did not present any favorable locations for H. This means that the filling order would be A_2B_2 follow by AB_3 , while the B_4 sites would remain empty. Among A_2B_2 sites, the most stable in $Zr(Cr_{0.5}Ni_{0.5})_2$ was the tetrahedra with composition $ZrZrCrCr$ presenting an H absorption energy value of -0.28 eV.

As it was expected, the total energy of the system decreased every time a hydrogen atom was absorbed. Total Energy per H atom is plotted in figure 5 a).

The computed cell volume also presents a remarkable trend after hydrogenation. It is well known that hydrogen absorption produces an increase in the size of the unit cell without changing the structure. The experimental observed volume expansion is, typically, in the order of $2.9 \text{ \AA}^3/\text{H}$ atom. Figure 5 b) shows the evolution of this parameter per H atom.

This trend would not be in accordance with experimental practices since Laves phases exhibit a ductile-brittle behaviour in normal operation conditions [20]. This field should be matter of further studies.

Finally, the Bulk Modulus (B) of a substance is an elastic property that indicates how easy a unit volume of fluid can be changed when changing the pressure working on it.

Is it defined as:

$$B = \frac{\partial P}{\partial V} V \quad (2)$$

where P is pressure and V , volume.

It also can be seen as an analogy with the Young's Modulus (E):

$$B = \frac{\Delta P}{\Delta V/V} \rightarrow \Delta P = B \frac{\Delta V}{V} \quad (3)$$

$$E = \frac{\sigma}{\Delta L/L} \rightarrow \sigma = E \frac{\Delta L}{L} \quad (4)$$

where σ is tensile stress and L , length.

The more resistant a solid is to compression, the more pressure it takes to change the volume and the larger the B modulus is.

As it is shown in Figure 5 c), no important changes were observed in this parameter. The variation range is between 150 and 165 GPa while the reported value for $ZrCr_2$ is around 176 GPa [21-22].

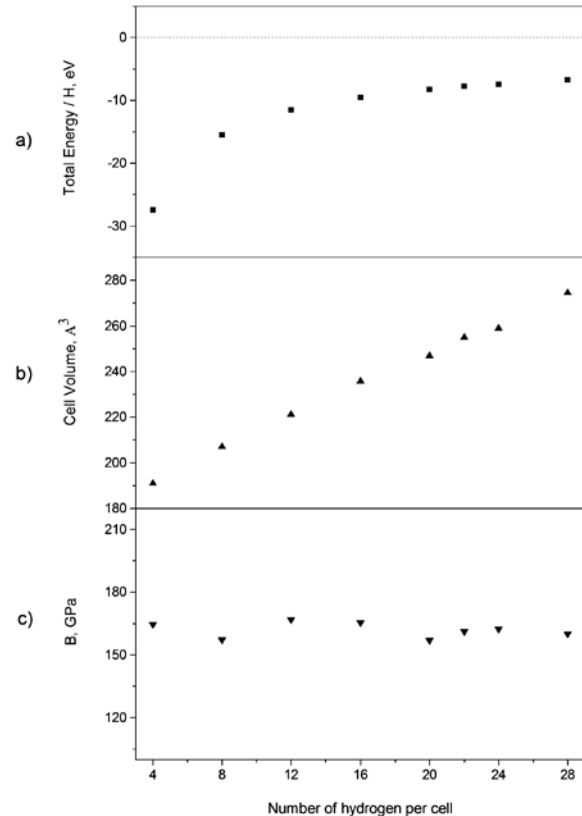


Figure 5 - a) Total energy; b) cell volume and c) Bulk modulus per number of hydrogen for $Zr(Cr_{0.5}Ni_{0.5})_2$ Laves phase.

CONCLUSIONS

The material science challenge in relation with hydrogen storage technologies is to understand the physic and chemistry interaction of hydrogen with other elements, in particular metals. Laves phases such as C14 $ZrCr_2$ and all its isostructural compounds, play an interesting role in the area and deserve a careful treatment.

In these lines, hydrogen absorption and the bulk modulus for $Zr(Cr_{0.5}Ni_{0.5})_2$ Laves phase have been described theoretically by means of DFT calculations. First-principles calculations, as the ones that have been performed here with VASP, can bring additional and complementary insights to lead to a better understanding of the hydrogenation processes and their dynamics.

This alloy exhibit a great hydrogen storage capacity, relatively high hydrogen absorption/desorption kinetics and a good cycle life. Besides, as it is composed by Ni to destabilize the hydrides, it can be use for technological applications.

However, more severe studies must be carried out to have a complete knowledge about the behaviour of the mechanical properties of this material, given the brittle nature that characterizes the Laves phases.

Computing Science is at the forefront of these requirements and at the service of researches who believe in its invaluable and complementary support.

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