



Trends of atomic Hydrogen absorption in Fe₂Zr Laves phases with ternary Additions: *Ab initio* study

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Abstract—The Pseudopotential Density Functional Theory (DFT) method using the Generalized Gradient Approximation (GGA) was applied to investigate hydrogen absorption trends in the cubic C15-Fe₂Zr Laves phase. We have determined the relative stability of atomic hydrogen at various interstitial sites. The results have been analyzed and particular attention was given to the formation and binding energies of Hydrogen atoms inside hydrides. It was found that hydrogen prefers the 96g site in the clean C15-Fe₂Zr compound and hydrogen absorption leads to a decrease of the heats of formation of the hydrides with occurrence of phase separation around 6H/fu. This fact was avoided by a presence of ternary additions. It has found that alloys containing Be, V, Cr, Mn, Y and Tc elements at the Fe sites can absorb up to 6H/fu. More interestingly, the hydrogen atoms cohesion in the hydride is found to be very sensitive to the third element nature and Hydrides with V, Y, and more particularly Tc and Ru exhibiting interesting energetics which would be very interesting for practical applications.

Keywords— Laves phases, relative stability, First-principles calculations, DFT and Hydrogen absorption.

I. INTRODUCTION

One kind of promising hydrogen storage materials are the Laves phases compounds with the AB₂ formula. These materials have reasonably high storage capacities, rapid kinetics and good cycling stability [1, 2]. The Laves phases can take the cubic C15 (MgCu₂), the hexagonal C14 (MgZn₂) or the dihexagonal C36 (MgNi₂) structures. Both the C14 and C15 have the ability to store high amounts of H when compared to C36 [1].

Among these Laves phase materials, the ZrFe₂ compound is a promising candidate for hydrogen storage and presents a potential for industrial applications [3]. Under ambient conditions, ZrFe₂ can absorb only a small amount of hydrogen to form a solid solution having a composition near ZrFe₂H_{0.16} [2]. Under pressure, the amount of absorbed hydrogen can be increased significantly and the formation of ZrFe₂H_{3.5} is possible [4]. However, these materials fail to meet the required practical use and gravimetric density criterions [5]. According to the USDOE, (United states department of Energy), only hydrogen storage media with 4.5 wt % reversible hydrogen capacity under affordable conditions should be established for commercial applications [5]. Currently, to the best of our knowledge no material has been found with properties fulfilling both gravimetric and thermodynamic criterions. So the search continues and new combinations of materials are proposed, prepared and tested experimentally for their hydrogen storage properties. But how do we propose new materials with the required thermodynamic properties? One method is by prediction of the desired properties by first-principles calculations and making slight modifications of the compound with metals with known properties. But the theoretical studies are still rather scares, and the discussion of the hydriding mechanisms and hydrogenation performances are often made in terms of (i) geometrical factors, (ii) volume size changes and (iii) enthalpies of formation. According to all that, this work aims at giving new insights on how the ternary transition metals addition can affect the hydrogen absorption trends in the C15-Fe₂ZrX system. To this purpose, quantum mechanics calculations are used to investigate the site occupancy, structural and magnetic properties of the Fe₂Zr after hydrogenation, within and without ternary addition and particular attention is given to the formation and binding energies of hydrogen atoms in the hydride.

II. COMPUTATIONAL DETAILS

All the calculations provided in this study were done using the density functional theory (DFT) using pseudopotential



methods as implemented in the pseudo-potential plane wave self-consistent field package (Quantum Espresso) [6]. The generalized gradient approximation (GGA) of Perdew et al. (PBE) [7] to the local density approximation was taken to include the exchange-correlation energy and ultra soft pseudo potentials of Vanderbilt were used [8]. These pseudo potentials explicitly treat the $[3s^23p^63d^64s^2]$ state of Fe and $[4s^24p^64d^25s^2]$ state of Zr as valence states. A Kinetic energy cut-off of 544 eV, and a well converged value of the k-point mesh over the Brillouin zone were considered. Namely, $8 \times 8 \times 8$ for the C15 structure, and $6 \times 6 \times 4$, $6 \times 6 \times 2$ for the C14 and C36 respectively. The electronic free energy was calculated using the marzari-vanderbilt cold smearing of 0.27 eV [9]. The cubic C15 structure was investigated in which three favorable types of tetrahedral sites for hydrogen location are usually considered, namely $8b$, $32e$ and $96g$. The difference between these sites is the type of atoms that constitute the tetrahedrons. Other sites, such as $48f$, $96h$ and $192i$ are not totally unoccupied and their probability of occupation could be increased under specific Thermodynamic conditions and in presence of ponctual defects such as ternary addition and vacancies. For this reason, all the sites are considered in this work, but only the most favorable ones were retained in the second part of the study.

III. RESULTS AND DISCUSSION

A. Clean Fe_2Zr

As a first step, a set of total energy/volume calculations was carried out for the clean Fe_2Zr alloy in the C14, C15 and C36 structures. For each structure, the nonmagnetic (NM) and ferromagnetic (FM) states have been considered. The corresponding values were fitted with the universal Birch-Murnaghan equation of state [10]. The lattice parameters, (c/a) ratios as well as the heats of formation for the Laves phases are presented in Table 1. The available experimental and theoretical data collected from the literature are also given in brackets.

Table 1: Lattices parameters (a), c/a ratios and heats of formation (ΔH_f) of Fe_2Zr compound in cubic-C15, hexagonal-C14 and di-hexagonal-C36 Laves phases.

		a (a.u.)	c/a	ΔH_f (eV)
C15	NM	13.06	1	-0.1099
	FM	13.35 (13.31) ^{11,12} (13.32) ¹³	1	-0.284 (-0.280) ¹³
C14	NM	9.19	1.66	-0.120
	FM	9.45 (9.45) ¹³	1.63 (1.624) ¹³	-0.271 (-0.265) ¹³
C36	NM	9.20	3.30	-0.114
	FM	9.44 (9.36) ^{11,12} (9.44) ¹³	3.26 (3.26) ^{11,12} (3.25) ¹³	-0.277 (-0.273) ¹³

As shown in Table 1, the predicted lattice parameters are consistent with X-ray diffraction measurements at room temperature [11-12] as well as with theoretical values [13]. In term of stability, the C15 structure with the FM state is the most stable ground state for Fe_2Zr . These results are in good agreement with previous theoretical and experimental ones [13, 14]. Consequently, only the ferromagnetic state with cubic C15 Laves phase has been considered for the detailed analysis given here.

B. Hydrogen Absorption in $C15-Fe_2Zr$

The relative stability of atomic hydrogen at the considered interstitial sites has been investigated while considering configurations with low and high H contents. For low H content, we have considered $Fe_2ZrH_{0.125}$ (using a primitive super-cell of C15 with 16Fe, 8Zr and 1H) and $Fe_2ZrH_{0.5}$ (a C15 unit-cell with 4Fe, 2Zr and 1H) alloys. Only one H atom (partial occupation) was positioned at the available Wyckoff positions of space group 227 (Fd-3m): $8b$, $16c$, $32e$, $48f$, $96h$, $96g$ and $192i$. For high H content, we have taken into account Fe_2ZrH_4 (a C15 unit-cell with 4Fe, 2Zr and 8H in $32e$) and Fe_2ZrH_6 (a C15 unit-cell with 4Fe, 2Zr and 12H in $48f$). The $32e$ and $48f$ sites were fully occupied by H atoms. The volume expansion, heats of formation and total magnetic moments after hydrogen absorption are given in the Table 2. The available experimental and theoretical values collected from the literature are also reported.

Table 2: Wyckoff positions of H atoms, volume variations, heats of formation and total magnetizations of Fe_2ZrH_x

	H positions	($\Delta V/V_0$) (%)	ΔH_f (eV/atom)	M (μ_B/Fe)
Fe_2Zr	Clean	0.00	-0.285	1.66
$Fe_2ZrH_{0.125}$	$8b$	0.94	-0.263	1.66
	$16c$	0.70	-0.223	1.72
	$32e$	0.69	-0.267	1.68
	$48f$	0.75	-0.265	1.70
	$96h$	0.88	-0.263	1.72
	$96g$	0.76	-0.270	1.71
	$192i$	0.76	-0.270	1.71
$Fe_2ZrH_{0.5}$	$8b$	-1.69	-0.068	0.00
	$16c$	5.08	-0.086	1.84
	$32e$	3.79	-0.227	1.69
	$48f$	3.19	-0.220	1.72
	$96h$	3.48	-0.214	1.81
	$96g$	1.89	-0.225	1.75
	$192i$	3.87	-0.238	1.78
$Fe_2ZrH_{3.5}$	-	24.30 ¹⁵	-	-
	-	22.60 ⁴	-	-
Fe_2ZrH_4	$32e$	19.48	-0.103	0.00
Fe_2ZrH_6	$48f$	39.10	-0.001	1.77



H in the 16c site has the highest value of -0.223 eV/atom. In term of stability, the Fe₂ZrH_{0.5} hydrides form also stable hydrides since their corresponding heats of formation are negatives. The preferred site for H remains the 192i site with the lowest energy of -0.238 eV/atom, followed by 32e and 96g. Comparatively, the 16c and 8b sites become much less favorable with increasing the H content. While the hydrogen insertion has generally caused a volume expansion that is higher in Fe₂ZrH_{0.5} than in Fe₂ZrH_{0.125}, the occupation of the 8b site has induced an unexpected decrease in the size of the unit cell by -1.69%. The higher expansion is obtained when H is on the 16c site (5.08 %). In the cases of large H amounts, the volume expansion is much noticeable for both Fe₂ZrH₄ and Fe₂ZrH₆, as seen by the values reaching almost 20 and 40% respectively. The predicted volume expansion in the case of Fe₂ZrH₄ is comparable to the literature ones given for Fe₂ZrH_{3.5} [4, 15]. Interestingly, the formation energies are higher than those predicted for low H contents, suggesting that additional absorption of H in Fe₂Zr leads to more unstable hydrides. This is due to the H-H distances in metal hydrides, where the H atom configurations and the repulsive H-H interactions determine the H capacity storage. Two criteria have been established in order to achieve the H absorption in metal hydride: (i) the geometrical condition, known as Switendick rule [16] which allows a H-H separation not less than 2.1 Å and (ii) the minimum hole size, known as the Westlake empirical rule, which has a value greater than 0.4 Å. The magnetic properties of the C15-Fe₂ZrH compounds are also affected by the hydrogen insertion. As it can be seen from Table 2, in comparison with value obtained for Fe₂Zr (1.66 μ_B/Fe atom), the magnetic moment of the compound increases with hydrogen insertion regardless of the nature of interstitial site. An unexpected behavior is however noticed in the case of H in 8b for Fe₂ZrH_{0.5} and Fe₂ZrH₄ where the magnetism of the hydride has totally disappeared due to the hydrogen insertion. Keeping in mind that the 8b site consists of 4 Fe atoms with very small interatomic distances, the H-Fe distance is predicted to be 1.49 Å, somewhat smaller than the sum of the two atomic radii r_{Fe} and r_H. Therefore, the hybridization between the s orbital of hydrogen with the d orbitals of Fe atoms induces strong interaction (bond) that reduces considerably the volume. Consequently, the d orbitals of Fe atoms are totally fulfilled, which explains the observed demagnetization.

IV. HYDROGEN ABSORPTION IN THE PRESENCE OF TERNARY ADDITIONS

we have considered the following elements: Be, Al, V, Cr, Mn, Co, Ni, Y, Tc and Ru. Our selection was motivated by the heat of formation values. Defected alloys with positive values or values close to zero were not considered for the hydrogenation analysis. We have also considered three

interstitial sites with the following Wyckoff positions: 32e, 48f and 96g sites. All these interstitial sites are fully occupied by H atoms. The corresponding alloy systems are Fe₂ZrH₄-X, Fe₂ZrH₆-X and Fe₂ZrH₁₂-X, respectively. It should be recalled however that, according to the Switendick rule [16], the above cited sites are not fully occupied in real materials. The 8b and 16c sites were not taken into account because of their least favorable formation energies (Table 2). The 192i sites are also not investigated according to their large (unphysical) volume expansion (80 %). Figs. 1(a), 1(b) give the variation of heats of formation, and hydrogen interaction energies, respectively. The presence of X in the Fe/Zr sites has been considered for three hydrogen contents: 4 H/f.u. (Fe₂ZrH₄-X), 6 H/f.u. (Fe₂ZrH₆-X) and 12 H/f.u. (Fe₂ZrH₁₂-X).

In Fig. 1(a), the dashed line refers to the heat of formation obtained for the clean C15-Fe₂Zr (-0.284 eV/atom). The heat of formation is very sensitive to both the hydrogen location and concentration. In Fe₂ZrH₄, when X substitutes Fe, the formation of hydrides is allowed for all ternary elements. However, when X substitutes Zr, the formation of Fe₂ZrH₄ is allowed only for Mn, Ni, Y and Ru additions while the remaining hydrides are unstable and the phase separation is favored. In Fe₂ZrH₆, the formation of hydrides is now only restricted to the Y doping when substitutes Zr. When the concentration in H increases further, it is not surprising to confirm that none of the Fe₂ZrH₁₂-X hydrides is favored.

Although the observed trends in heats of formation and absorption energies are highly dependent on the H-H distances and the interstitial hole size, the interaction between H atoms in the bulk is also a key parameter. Consequently, this essential parameter is investigated here for all alloys and the interaction energy is compared in the case of H atoms in clean Fe₂Zr. The obtained results can be used in thermodynamic models that can better understand the absorption/desorption mechanism in the storage process of H in solids. As shown in Fig. 1(b), the interaction energies are very sensitive to the H amounts as well as to the nature of the third element addition. For Fe₂ZrH₄ and Fe₂ZrH₆ hydrides, the H atoms exhibit attractive interaction and prefer the atomic form for all the ternary elements that substitute Fe. In particular, a strong H attraction is noticed in the Fe₂ZrH₄ hydride when V, Co and Y substitute Fe. However, the scheme is more complex for the Zr substitutions. For example, when Al substitutes Zr, repulsive interactions are observed for the Fe₂ZrH₄ and Fe₂ZrH₆ hydrides. Comparatively, Co substitution induces respectively repulsive and attractive interactions for Fe₂ZrH₆ and Fe₂ZrH₄ while an opposite behavior is noticed for Tc. In the case of Fe₂ZrH₁₂, in good agreement with the positive heat of formations reported in Fig. 1(a), the H atoms generally show a strong repulsive interaction and tend to form H₂ molecules. Interesting exceptions are obtained in the cases of Y, Tc and Ru. The



addition of Y induces fairly low repulsive interaction whereas, with the additions of Tc and Ru, attractive interactions are created in the presence of high H amount (12 H/f.u.). This is very important and promising in H absorption. This means that the energetics of H absorption in Fe₂Zr alloys with ternary additions is governed by the H cohesion/decohesion behavior. The obtained results will be discussed and further aspects will be given in the next section.

V. CONCLUSIONS

The aim of this work was to use the DFT pseudopotential method to investigate the Hydrogen absorption trends in C15-Fe₂Zr Laves phases without and within ternary additions. The main results can be summarized as follows.

The Fe₂Zr compound is more stable in the C15 Laves structure with a ferromagnetic state, and the predicted cell parameters are in good agreement with the available experimental results. From site preference analysis, The site preference of hydrogen atoms depends on the hydrogen concentrations. For 0.125 H/f.u., hydrogen prefers 96g site, while it is also favorable in the 48f one with 0.5 H/f.u. For high H contents, the hydrogen absorption leads to a decrease of heats of formation of the hydrides with occurrence of phase separation around 6H/fu. Moreover, the total magnetizations are also affected with vanishing magnetism for 0.5H/fu and 4H/fu when H atoms are located at 8b and 32e respectively. This fact is correlated with the local environment of the 8b and 32e sites made up of 4 Fe for the former, and Zr and 3Fe atoms for the later. These trends are also affected by ternary elements presence. The alloys with Be, V, Cr, Mn, Y and Tc elements at the Fe sites can absorb up to 6H/fu. More interestingly, the hydrogen atoms cohesion in the hydride is found to be very sensitive to the third element nature and Hydrides with V, Y, and more particularly Tc and Ru exhibit interesting energetics which would be very interesting for practical applications.

VI. REFERENCES

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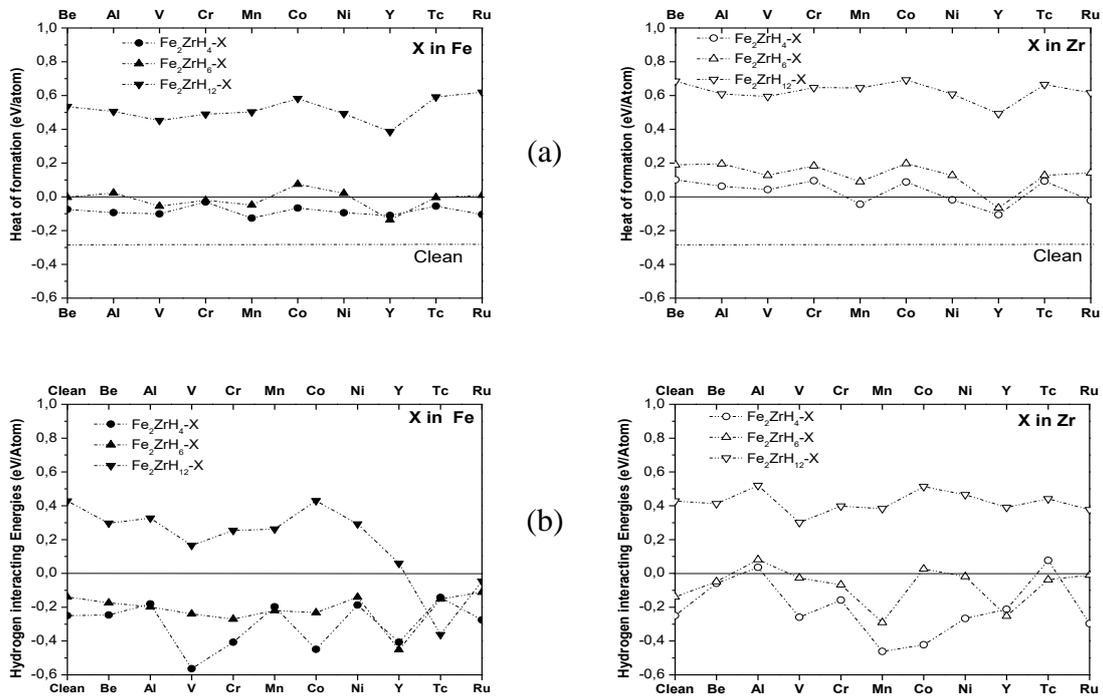


Figure 1: Variation with X ternary element of (a) heats of formation, and (b) interacting energies of the Fe_2ZrXH_n hydride when X substitute Fe Atom and X substitute Zr Atom.

