



Research articles

Theoretical study of YFe_2H_x ($x = 0-5$): A comparison between cubic and orthorhombic phasesShu-Rong Yuan^a, Liuzhang Ouyang^{b,c}, Min Zhu^{b,c}, Yu-Jun Zhao^{a,b,*}^a Department of Physics, South China University of Technology, Guangzhou, Guangdong 510640, China^b Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, South China University of Technology, Guangzhou, Guangdong 510640, China^c School of Materials Science and Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

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ABSTRACT

The stability of binary intermetallic Laves phase YFe_2 and its hydride YFe_2H_x ($x = 0-5$) are studied using first-principles calculation. Accompanied with the analysis of the hydrogen binding energy and the formation enthalpy in various interstitial sites in YFe_2H_x , a transition of the stability from cubic to orthorhombic phase is found when hydrogen concentration increases to 1.5H/f.u. It is found that the hydrogen binding energy is very sensitive to the magnetic property of neighboring atoms. To get a further insight of the transition, we take into account external strains, as well as chemical substitution at Y site. It turns out that the transition point can be tuned by strain and chemical bonding.

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1. Introduction

Laves phases are the largest group of intermetallic compounds, and have attracted great attentions, since Laves firstly showed us the highlights of the characteristics of this intermetallic family [1]. They are popular candidates in industrial production, especially in hydrogen energy industry, due to their unique structural, mechanical and magnetic properties [2–10]. Some particular Laves phases have high hydrogen-absorption/desorption kinetics, and considerable hydrogen storage capacity thanks to the many interstitial sites for the insertion of hydrogen [1], allowing them to be competitive hydrogen storage materials.

In spite of all these advantages Laves phases have in hydrogen storage aspect, the structural instability still places them in a dilemma about their industrial application. Laves phase AB_2 may have the structure of C15 cubic, C14 hexagonal or C36 dihexagonal type, depending on the stacking types of layers of A and B atoms [2]. The energy differences of these three types can be very small due to the close structural relation [11]. Hence, two or even three polytypes of a particular pure Laves phase can be found coexisting or transforming from one to another without much difficulty, let alone the alloy cases. Take YFe_2 , a typical ferromagnetic Laves phase, as an example. It is known to have C15 cubic structure at

normal pressure and temperature, and may transform to the hexagonal type within a high pressure [12]. Once alloyed with some particular intermetallic compounds, say YAl_2 , another C15 Laves phase, the crystal could also transform from the previous C15 cubic type to C14 hexagonal one, then back to the cubic structure, along with the addition of YAl_2 content [13–21]. When hydrogen is introduced, the lattice distortion-induced transition is reported to be more diverse and no longer limited to the cubic or hexagonal phase. Depending on the preparation conditions and the hydrogen storage amount, the cubic YFe_2 may transform into variant crystal structures after the absorption of hydrogen. $\text{YFe}_2\text{H}_{1.75}$ is found to be cubic, while $\text{YFe}_2\text{H}_{1.2}$ and $\text{YFe}_2\text{H}_{1.9}$ are reported to be tetragonal by V. Paul-boncour and co-workers [22]. $\text{YFe}_2\text{H}_{2.4}$ was found to be rhombohedral by Kanematsu [23], who also reported YFe_2H_4 to be orthorhombic [24], which, however, had been reported to be cubic by Buschow et al. earlier [25]. $\text{YFe}_2\text{H}_{2.6}$ is found to be cubic though there is local distortion [26]. $\text{YFe}_2\text{H}_{3.5}$ is reported to be monoclinic [27]. For $\text{YFe}_2\text{H}_{4.2}$, along with the increase of the temperature, a progressive transformation from monoclinic to rhombohedral and then cubic has been observed [28,29]. The saturated YFe_2H_5 is reported to have the structure of orthorhombic [30,31]. With all these different hydride phases reported by different research groups, controversies still remain about the structural stability. For a better application of YFe_2 as hydrogen storage material technically, we have to deal with this stability problem.

* Corresponding author at: South China University of Technology, Department of Physics, 381 Wushan Rd, Guangzhou, Guangdong 510640, China.

E-mail address: zhaoyj@scut.edu.cn (Y.-J. Zhao).

It would surely provide more complete information to investigate the transition with as many phases as possible considered for the overall H content range. However, there are a large amount of possible phases found experimentally for YFe₂ hydrides, like rhombohedral, tetragonal, and monoclinic. Besides, the configuration may also transform between phases along with the change of temperature. In addition, even for one specific phase, there may be structures with different space groups. Therefore, an investigation on the H-eliminated cubic and H-saturated orthorhombic phases of YFe₂H_x with variation of hydrogen concentration would present a qualitative picture of the stability transition with feasible computational efforts.

In this work, we investigate YFe₂H_x in pristine cubic phase and orthorhombic phase using first-principles calculations. It is found that the stability transition takes place around $x = 1.5$, and the hydrogen binding energy strongly depends on the magnetism of nearby host atoms. Our investigation with external pressure and chemical substitution reveals that the transition point is clearly associated with the strain and chemical bonding of the component elements.

2. Computational details

The calculations are performed based on first-principles density functional theory, as implemented in the Vienna ab initio Simulation Package [32,33]. With the use of projector-augmented wave potentials [34,35], the exchange-correlation interactions are simulated by the generalized gradient approximation using Perdew-Burke-Ernzerhof scheme [36]. The energy cutoff for the plane-wave basis set is 450 eV, except for the strain case. Hydrostatic pressure is adopted to simulate the external strain with a larger energy cutoff of 500 eV to guarantee the precision for the distortion between cubic and orthorhombic phases. The Monkhorst-Pack k-point meshes of $7 \times 7 \times 7$ and $9 \times 9 \times 7$ are used for the cubic and orthorhombic YFe₂H_x, the adopted distorted phase, respectively. For the structural optimization, all the structures in our calculations are fully relaxed until the change in the energy between two ionic steps is smaller than 1 meV.

Our analysis about the stability comparison of the two phases is mostly based on calculations of the binding energy and the formation enthalpy.

The binding energy of hydrogen is calculated by the equation

$$E_{\text{binding}} = 1/x(E_{\text{AB}_2\text{H}_x} - E_{\text{AB}_2}) - E_{\text{H}_2}/2,$$

where $E_{\text{AB}_2\text{H}_x}$ is the energy of the hydride AB₂H_x, E_{AB_2} the energy of the Laves phase AB₂, and E_{H_2} the energy of hydrogen molecule.

The formation enthalpy is calculated by the equation

$$\Delta H_{\text{formation}} = E_{\text{AB}_2\text{H}_x} - E_{\text{A}}^{\text{bulk}} - 2E_{\text{B}}^{\text{bulk}} - x\mu_{\text{H}}, \quad (1)$$

where $E_{\text{A}}^{\text{bulk}}$ and $E_{\text{B}}^{\text{bulk}}$ are the energy of A and B element in bulk phases, respectively, and the chemical potential of hydrogen μ_{H} is given respect to the H₂ molecule, i.e., $\mu_{\text{H}} = \mu_{\text{H}_2}/2 + \Delta\mu_{\text{H}}$.

3. Structure of YFe₂ and YFe₂H_x

The C15 Laves phase compound YFe₂ has a space group of *Fd-3m* with 8 yttrium atoms and 16 iron atoms locating at 8a and 16d Wyckoff site respectively in its conventional cubic cell, as shown in Fig. 1. In this unit cell, there are three types of tetrahedral interstitial sites for the insertion of hydrogen, namely A₂B₂, A₁B₃ and B₄, with the number of 96, 32 and 8, respectively. A₂B₂ tetrahedral site is also named as 96g Wyckoff site, where H atom is surrounded by 2 A atoms (here Y) and 2B atoms (here Fe). In the A₁B₃ site (or 32e site), H is surrounded by 1 A and 3B atoms. As for the B₄

site (or 8b site), H is at a regular tetrahedron with 4B atoms in the corners. Despite a totally 17 tetrahedral sites per YFe₂ formula, the experimentally reported hydrogen storage capacity of YFe₂ turns out to an extent of 5H/f.u. [37], probably due to the Switendick criterion [38], which states that the distance between H atoms should be no less than 2.1 Å. In this work, the hydrides YFe₂H_x is investigated with x ranging from 0 to 5.

To simulate the hydrides YFe₂H_x within the C15 structure, hydrogen atoms are inserted successively into the conventional cubic cell of YFe₂ until the system is saturated with H atoms. To determine the preferential absorption sites, we set the all three individual interstitials as well as the mixed cases as functions of the concentration of hydrogen for per YFe₂ formula. Taking Switendick criterion into account, we distribute these foreign atoms in a way to maximize their distance in order to minimize the repulsive interaction between them.

For the orthorhombic phase YFe₂H₅ [31], it crystallizes in the *Pmn21* space group with lattice constants of $a = 5.437$ Å, $b = 5.850$ Å, and $c = 8.083$ Å (Fig. 1). Before the dehydrogenation calculation, the magnetic property of YFe₂H₅ needs to be determined first. The stability comparison calculation between the paramagnetic and ferromagnetic orthorhombic YFe₂H₅ shows that the paramagnetic YFe₂H₅ is more stable, in agreement with the previous results. The orthorhombic YFe₂H₅ contains two kinds of inserted hydrogen, A₂B₂ and A₁B₃, with the hydrogen amount of 4/f.u. and 1/f.u., respectively. As opposed to the above cubic case where hydrogen atoms are added to the pristine C15 YFe₂, we will remove the hydrogen atoms progressively from YFe₂H₅ until the system is free of them.

4. YFe₂H_x in cubic phase

We first focus on the hydrides YFe₂H_x within the pristine C15 structure, and study about the stabilities as hydrogen inserts into three different interstitial sites. The calculated binding energy of hydrogen is shown in Fig. 2. Note that the quantities of these three kinds of sites are different from each other, so while the numbers of hydrogen atoms inserted into A₂B₂ and A₁B₃ can reach as much as 5 and 4, respectively for every YFe₂ formula, the capacity limited to B₄ sites is only 1 per YFe₂.

One may notice that the calculated binding energy is always negative, meaning a spontaneous absorption of H for the overall H content in H-rich condition. Especially, at $x = 0.5$, the H binding for B₄ case is the strongest (0.5 eV/H), avoiding the possibility of phase separation from it. The calculated zero-point energy of H at B₄ site is less than 0.2 eV, which hardly destabilizes the configuration.

Meanwhile, many previous experimental researches have observed that in the YFe₂ system, the most favorable interstitial site for hydrogen is always A₂B₂, and B₄ site absorbs least or even no hydrogen atom, which is mostly ascribed to the largest inter-space of A₂B₂ site and the smallest of B₄ [28,31,39]. From Fig. 2, however, we find that the most stable site among all the three varies along with the hydrogen concentration. At the initial stage of the hydrogen absorption process, B₄ is surprisingly found to be the most stable one, and A₂B₂ ranks the third; once the concentration of hydrogen reaches 0.75/f.u., A₁B₃ replaces B₄ to become the most favorable one; the trend changes again after 1.5H/f.u. are introduced, and only from then on does A₂B₂ become the most stable interstitial site.

We notice that all these variations of stability take place before H concentration of 1.5/f.u. Interestingly, the YFe₂ hydride with the lowest H content was reported to be YFe₂H_{1.2} experimentally. As we have considered the impact of zero-point energy and magnetic configuration (see below in this section), it leaves an open question

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