# Structural and electronic properties of the ternary intermetallic hydride TiFeH from *ab-initio* calculations

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#### ABSTRACT

The stability and electronic structure of orthorhombic hydride TiFeH were investigated using the first principles "full-potential linearized augmented plane-wave method" based on density functional theory calculations. We have investigated the lattice parameters, bulk modulus, the electronic structure and the formation energy of the ternary TiFeH hydride in its ground state. The Fermi level of TiFeH hydride falls slightly below that of TiFe. Total and partial DOS analysis reveals that the TiFeH hydride has a metallic character and the hybridization between iron 3d and hydrogen 1s states appear to be the strongest. The electron density shows that a relatively high electron density extends from the hydrogen atom site to the iron atom site, but not to the titanium atom site which is a very important characteristic in hydrogen storage applications. Its formation energy differs from that in literature.

KEYWORDS: First principles; Density function theory; TiFeH hydride; DOS analysis; Formation energy.

#### **1. Introduction**

Hydrogen is a clean and renewable fuel for future transportation and energy storage. A promising approach for hydrogen storage is the solid-state storage where H atoms are incorporated in the lattice of the host material. The experimental results of the formation energies of binary metal hydride show that these cover a wide range in stability going from the highly stable hydrides  $(\Delta E_f \ll 0)$  of the alkali metals, alkaline earth metals, rare earth metals and early transition metals, to the much less stable hydrides of the metals around the middle of the transition metals ( $\Delta E_f < 0$ ), and to the unstable hydrides of the late transition metals ( $\Delta E_f > 0$ ) [1]. Up to now, none of the binary metal hydrides fulfills both the hydrogen density and the thermodynamic stability criteria. The search for better hydrogen storage and intermediate thermodynamic stability materials continues among the ternary metal hydrides. The intermetallic compound TiFe, which crystallizes in the cubic CsCl-type structure [2] absorbs reversibly up to 1.8 wt% hydrogen to form the orthorhombic TiFeH hydride. Fischer et al. [3] and Thompson et al. [4] investigated experimentally TiFeH and found an orthorhombic symmetry for the crystal structure. Many investigations by the DV- $X_{\alpha}$  cluster method on TiFe hydrides were carried out in the past [5-9] to determine the metal-hydrogen bonding. Gupta studied electronic structure of TiFeH using an augmented plane wave (APW) method where the crystal potential was constructed using Slater's local exchange approximation [10]. Results were presented on the electronic properties of  $\beta$ -TiFeH and compared with the electronic structure of pure TiFe. Kinaci et al. investigated the TiFeH hydride based on a pseudopotential method within the generalized gradient approximation [11]. Formation energy and density of states of TiFeH hydride were calculated. In the present work we have performed first principles DFT electronic calculations of TiFeH using full-potential linearized augmented planewave method (FP-LAPW) to determine its structural and electronic properties. We have compared the electronic structure of the TiFeH with the one of pure TiFe. There are some differences with the results found by Gupta in terms of the Fermi level position between TiFeH and TiFe. The calculated formation energy of the ternary TiFeH hydride, which differs from the value obtained by Kinaci et al., is somewhere between those of the two constituent binary hydrides (TiH<sub>2</sub> and FeH) satisfying therefore the criterion for hydrogen desorption in PEM fuel cells.

## 2. Computational details

TiFeH has an orthorhombic structure and a  $P_{222_1}$  (17) space group, as shown in Figure 1 [3]. The TiFeH structure is characterized by octahedral framework sites occupied by H atoms of type Ti<sub>4</sub>Fe<sub>2</sub>. The atomic coordinates are: titanium in 2d (0.5, 0.757, 0.25), iron in 2c (0, 0.2941, 0.25), and H in 2a (0, 0, 0). All calculations have been done using the full-potential linearized augmented plane wave (FP-LAPW) method based on the density functional theory (DFT), as implemented in the Wien2k code [12]. The exchange-correlation interaction was treated within generalized gradient approximation (GGA) of Perdew et al. [13]. The Kohn-Sham equations are solved self-consistently by choosing the muffin-tin radii (MT) to be 1.8, 1.8 and 1.3 a.u for Ti, Fe and H, respectively. The core states were treated fully relativistically, while the valence states (3s, 3p, 3d and 4s) were treated within the scalar relativistic approximation. The spin-orbit interaction was not included in our calculations. The threshold energy between valence and core states was -7eV. Taking a convergence energy of  $10^{-4}$ Ry, the  $R_{MT}K_{max}$  and number of k-point parameters were optimized to be 9 and 3000 k-points, respectively.



Figure 1: TiFeH (P<sub>2221</sub>) orthorhombic structure

# 3. Results and discussion

## **3.1 Structural analysis**

By fitting the total energy versus volume data to the non-linear Murnaghan equation of state [14], as shown in Figure 2, we obtained the lattice parameters, the value of the bulk modulus and its pressure derivative for both TiFe and TiFeH (Table 1). The equilibrium lattice parameters calculated for TiFe and its hydride TiFeH are close to the available experimental data and previous theoretical calculations, as shown in Table 1.

## **3.2 Band structure and density of states analyses**

As seen from the band structures of TiFe and TiFeH shown in Figure 3, both TiFe and its hydride have a metallic character because of the absence of gap at the Fermi level. The addition of hydrogen atom to the unit cell increases the number of energy bands in first Brillouin zone. Comparing the DOS structure of TiFeH to that of TiFe (Figure 4), we found that the DOS structure of TiFeH shifts slightly towards bonding states at lower energies compared to that of pure TiFe. In the latter, the Fermi level ( $E_F = 0.89624$  Ry) falls in a valley of the density of states, characteristic of b.c.c. metals, which separates Ti-Fe bonding from Ti-Fe antibonding manifolds.

Table 1: Calculated lattice constants, bulk modulus, pressure derivative B' (in bold) compared to	to
experimental data and other works on the TiFe and TiFeH when available	

Hydride	Reference	Method	approximation	Calculated cell parameters (Å)			B (GPa)	B'
_				Α	В	С		
TiFe	Present	FP-LAPW	GGA-96	2.959	2.959	2.959	361.3996	-22.6742
	[2]	Experimental	Experimental	2.978	2.978	2.978	/	/
	[11]	PP-PW	GGA-99	3.011	3.011	3.011	/	/
TiFeH	Present	FP-LAPW	GGA-96	2.932	4.515	4.276	178.8451	-0.2786
	[3]	Experimental	experimental	2.966	4.522	4.370	/	/
	[4]	Experimental	experimental	2.956	4.543	4.388	/	/
	[15]	PAW	GGA-96	2.889	4.529	4.264	/	/
	[11]	PP-PW	GGA-99	2.978	4.549	4.417	/	/





In the TiFeH hydride, the Fermi level ( $E_F = 0.89394 \text{ Ry}$ ) falls slightly below that of TiFe whereas Gupta found a shift towards higher energies. We also observe the presence of a structure at low energy, centered at about -8 eV below  $E_F$ , which results from the metal-hydrogen bonding. Figure 5-a shows that the contribution of total DOS of Fe dominates in the energy range from - 4 eV to 1 eV which is mostly responsible for structural bonding. Most anti-bonding states are described by total DOS of Ti above the 1 eV. The contribution of total DOS of H is roughly limited to the low energy range from -10 eV to -6 eV. The partial density of states of both Ti and Fe reveals that 3d states density predominates, as shown in Figures. 5-b and 5-c. The hybridization reaction between 3d Fe and 1s H is stronger than 3d Ti and 1s H which is a very important feature of the hydrogen storage compounds (Figures 5-d and 5-e).

## **3.3 Electron density analysis**

According to the contour maps of electron density distributions on TiFeH atomic planes in Fig. 6, we observe that high electron densities extend from the iron atom to the hydrogen atom, but not to the titanium atom. In metal-hydrogen systems, the titanium atom has ordinarily a larger affinity to hydrogen than iron atoms. This confusing result is due to the fact that this kind of chemical bond

between iron and hydrogen seems to be one of the important characteristics of the hydrogen storage compounds. Similar results are also found in other hydrogen storage compounds [16, 17].



Figure 3: Band structure of both a) TiFe and b) TiFeH.



Figure 4: Total DOS of both a) TiFe and b) TiFeH.



Figure 5: Total and partial density of states of a) TiFeH tot, Ti tot, Fe tot and H tot, b) Ti (tot, s, p, and d), c) Fe (tot, s, p, and d), d) Ti tot and H tot, and e) Fe tot and H tot.



Figure 6: Contour maps of the electron density distributions on the a)  $(\bar{1}00)$  and b) (011) atomic planes of TiFeH.

#### 3.4 Formation energy

Based on the following general reaction equation describing the reaction of  $H_2$  gaz with the TiFe alloy:

$$TiFe + \frac{1}{2}H_2 \to TiFeH \tag{1}$$

From the view of thermodynamics, a lower formation energy defined as the total energy difference between the compound and its constituents means better forming ability. The formation energy of TiFe is calculated as:

$$E_f = \left( E_{tot}(TiFeH) - E_{tot}(TiFe) - \frac{1}{2} E_{tot}(H_2) \right)$$
(2)

Where  $E_{tot}$  (TiFeH),  $E_{tot}$  (TiFe) and  $E_{tot}$  (H<sub>2</sub>) are the total energies of TiFeH, TiFe and H<sub>2</sub>, respectively. The  $E_{tot}$  (H<sub>2</sub>) taken in this calculation was 2.32 Ry [18-22]. The formation energy of TiFeH is calculated and equals - 45.08 kJ/mol H<sub>2</sub>. This latter value shows that the formation energy of the TiFeH ternary hydride is somewhere between those of the two constituents' binary hydrides (TiH<sub>2</sub>,  $E_{f}$ = -76 kJ/mol H<sub>2</sub> [23]) and (FeH,  $E_{f}$ = 15.8 kJ/mol H<sub>2</sub> [24]), and satisfies  $E_{f}$  > -48 kJ/mol H<sub>2</sub>, the criterion for hydrogen desorption below 100 °C [25]. This criterion is the ultimate goal if hydrogen storage in metal hydrides should be used in conjunction with a polymer electrolyte membrane (PEM) fuel cell. The formation energy obtained by Kinaci et *al.* was - 21.9 kJ/mol H<sub>2</sub>, which is less considerably than that in our calculations. In their calculations, the formation energy was not that of absolute value of real formation energy.

#### 4. Conclusion

The calculated equilibrium lattice parameters of TiFe and its hydride TiFeH are close to the available experimental data and previous theoretical calculations. The TiFeH hydride has a metallic character and the insertion of a hydrogen atom to the unit cell increases the number of energy bands in the first Brillouin zone. The Fermi level falls slightly below that of TiFe whereas Gupta found a shift towards higher energies. Iron is the main contributor to bond formation in the TiFeH hydride, especially with hydrogen. The hybridization reaction between 3d Fe and 1s H is stronger than between 3d Ti and 1s H which is a very important feature for hydrogen storage compounds. The high electron density extends from the iron atom to the hydrogen atom, but not to the titanium atom due to the larger affinity between hydrogen and iron atoms rather than hydrogen and titanium atoms in the TiFeH compound. Therefore, this kind of chemical bond seems to be an important characteristic of hydrogen storage compounds. The formation energy of the TiFeH ternary hydride differs considerably from that obtained by Kinaci et *al.*. It is somewhere between those of the two constituents' binary hydride (TiH<sub>2</sub> and FeH), and verify H<sub>f</sub> > -48 kJ/mol H<sub>2</sub>, the criterion for possible hydrogen desorption below 100°C in PEM fuel cells.

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