Ab initio investigation of FeTi–H system

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Received 5 October 2006; accepted 6 October 2006
Available online 6 December 2006

Abstract

In this study, a first principles search for a possible hydride with high hydrogen storage capacity was carried out in the FeTi intermetallic system. In this regard, formation energies of FeTiH<sub>x</sub> (x = 1–6) hydrides are systematically investigated on the basis of crystal and electronic structures and structural stability. Total energies were calculated by ab initio pseudopotential method within the generalized gradient approximation (GGA) to density functional theory (DFT). In the stability analysis, mostly the subgroups of the space group of the FeTi structure (P<sub>m</sub>3<sub>m</sub>) as well as some special cases in which Fe–Ti coordination is similar to P<sub>m</sub>3<sub>m</sub> were considered. Our calculations predicted the experimental structures of FeTiH and FeTiH<sub>2</sub>. It was found that, the insertion of hydrogen into the structure causes an increased electron density in the electronic orbitals of Fe which were oriented towards hydrogen atoms. We have also identified a new hydride which is less stable than the experimentally observed ones, having four hydrogen atoms per chemical formula.

Keywords: Intermetallic hydrides; Hydrogen storage; First principles simulation

1. Introduction

Today, hydrogen is considered to be one of the most promising energy sources that may solve the energy problem. Unlike the diminishing fossil fuels, hydrogen does not produce any polluting or green house gases or toxic chemicals but water. However, the practical usage of hydrogen as an energy source depends on the ease of storability and portability. This requirement makes the storage in solid state much more important. In this sense, many metallic hydrides based on intermetallic compounds become applicable over the years.

Ivey and Northwood [1] reviewed many binary metal alloy systems that have been studied so far including AB, AB<sub>2</sub>, AB<sub>3</sub>, AB<sub>5</sub> and A<sub>2</sub>B<sub>7</sub>. AB<sub>3</sub> intermetallics store 1.4–1.9 wt% hydrogen, with fast reaction kinetics and the resulting hydrides are relatively stable. In AB<sub>2</sub> type, 1.5–2.0 wt% hydrogen can be stored with fast kinetics producing stable hydrides. AB<sub>5</sub> and A<sub>2</sub>B<sub>7</sub>-type intermetallics can store 1.6 wt% in stable hydrides. Mg-based compounds can store up to 7% hydrogen by weight and the resulting hydrides are stable however kinetic problems exist. AB-type intermetallics can store 1.8% hydrogen by weight with medium kinetics and the stability of the hydrides varies.

Among AB intermetallics, FeTi system was studied various times due to its moderate kinetics with relatively high equilibrium hydrogen pressure (≈ 4.5 atm) at room temperature. However, low storage capacity (1.8–1.9 wt%) and O<sub>2</sub>, H<sub>2</sub>O, CO poisoning problems could not be resolved fully in order to use in practical applications. FeTi has CsCl-type structure which corresponds to P<sub>m</sub>3<sub>m</sub> space group with a lattice parameter of 2.9789 Å [2]. Reilly and Wishwall [3] observed that FeTi reacts readily to form FeTiH<sub>1.04</sub> (β phase) and FeTiH<sub>1.95</sub> (γ phase) according to reactions:

2.13FeTiH<sub>0.1</sub>(x) + H<sub>2</sub> → 2.13FeTiH<sub>1.04</sub>(β)

followed by

2.20FeTiH<sub>1.04</sub>(β) + H<sub>2</sub> → 2.20FeTiH<sub>1.95</sub>(γ).

They also showed that the absorption isotherms of pressure vs. composition are several atmospheres higher than desorption isotherms at the same composition causing the so-called
Table 1
Experimental data available for the FeTi–hydrides

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Reference</th>
<th>Structure</th>
<th>Cell parameters</th>
<th>Space group</th>
</tr>
</thead>
</table>
| FeTiH$_{−1}$ ($β$) | Reilly and Wishwall [3] | Tetragonal | $a = 3.18$ Å  
$c = 8.73$ Å | No. 62, No. 26, No. 17, No. 28 |
|             | Thompson et al. [5]   | Orthorhombic | $a = 2.956 \pm 0.004$ Å  
$b = 4.543 \pm 0.006$ Å  
$c = 4.388 \pm 0.006$ Å | No. 17 |
|             | Fischer et al. [27]   | Orthorhombic | $a = 2.966$ Å  
$b = 4.522$ Å  
$c = 4.370$ Å | No. 65 |
| FeTiH$_{−2}$ ($γ$) | Reilly and Wishwall [3] | Cubic | $a = 6.61$ Å  
$b = 4.7044 \pm 0.0012$ Å  
$c = 2.8301 \pm 0.0005$ Å  
$β = 96.97 \pm 0.05^\circ$ | No. 10 |
|             | Thompson et al. [6]   | Orthorhombic | $a = 7.041$ Å  
$b = 6.234$ Å  
$c = 2.828$ Å | No. 65 |
|             | Fischer et al. [8]    | Orthorhombic | $a = 7.029$ Å  
$b = 6.233$ Å  
$c = 2.835$ Å | No. 65 |

Table 2
The definition of the structures used in this study, giving the space groups and Wyckoff positions of the atoms within the unit cells

<table>
<thead>
<tr>
<th>Space group</th>
<th>Fe Ti H/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 (unique axis $b$)</td>
<td>2m 2n 1a + 1d + 1f + 1g</td>
</tr>
<tr>
<td>17$^a$</td>
<td>2c 2d 2a 4e, 4f, 4g, 4h, 4i, 4j, 4k, 2b + 2d</td>
</tr>
<tr>
<td>65</td>
<td>2a 2c 2b, 2d 4g + 4i, 4g + 4j, 4h + 4l</td>
</tr>
<tr>
<td>65$^b$</td>
<td>2a + 2c + 4e</td>
</tr>
<tr>
<td>123</td>
<td>1a 1d 1b, 1c 2e, 2f, 2g, 2h, 2c</td>
</tr>
<tr>
<td>135</td>
<td>1a 1b 1b + 1c</td>
</tr>
<tr>
<td>166</td>
<td>1a 1b 1b + 2f, 2e, 2f, 2g, 2h</td>
</tr>
<tr>
<td>200</td>
<td>6f, 6g</td>
</tr>
<tr>
<td>215</td>
<td>4</td>
</tr>
<tr>
<td>221</td>
<td>3c, 3d</td>
</tr>
</tbody>
</table>

Total number of structures calculated is 43. $^a$ and $^b$ are experimental structures according to [5,6,8,27], respectively.

hysteresis effect. Moreover, the shapes of these isotherms are very sensitive to increase in Ti amount above 45.9–48.2 wt% Ti.

Reidinger et al. [4] claimed that phases present in a given FeTiH$_{x}$ sample depends on the method of preparation and the sample history thus producing a hysteresis effect. They suggested that $β_1$ (FeTiH$_{−1}$) phase coexists with $γ$ phase during hydrogen desorption on the other hand $β_2$ (FeTiH$_{−1,4}$) phase coexists with $γ$ phase during hydrogen absorption. Thompson et al. [5–7], in their consecutive studies, provided the possible crystal structures and atomic positions for the solid solution of FeTi–H ($α$ phase) and the two known hydrides FeTiH$_{−1}$ ($β$ phase) and FeTiH$_{−2}$ ($γ$ phase). Fischer et al. [8] investigated FeTiH$_{1,4}$ assuming an orthorhombic symmetry for the crystal structure. They identified Ti$_4$Fe$_2$ and Ti$_2$Fe$_4$ octahedral sites for deuterium. Ti$_4$Fe$_2$ sites are 100% and Ti$_2$Fe$_4$ sites are 91% occupied by deuterium. The proposed crystallographic parameters for the FeTiH$_{−1}$ ($β$) and FeTiH$_{−2}$ ($γ$) phases were summarized in Table 1.

In addition to experimental studies, theoretical modeling techniques became widely used in accordance with the developments in computer technology. Computational science can provide reliable and in-depth information about the system
under consideration. Computational methods can even be applied to phenomena where practice is impossible, as long as the sufficient theoretical information is present. Moreover, a full control on the system variables can be achieved and thus effects of the parameters on the results can easily be determined. First principles calculations based on quantum theory have successfully been used in predicting physical properties (lattice constants, bulk modulus, dielectric properties, etc.) of the systems at their ground states.

In the last 15 years, the electronic band structures of metallic hydrides along with the energy for hydride formation have been studied with first principles total energy pseudopotential methods. Min and Ho [9] studied hydrogen diffusion in yttrium and calculated formation and activation energy for diffusion. They also showed the consistency of their results with the experimental data. Smithson et al. [10] presented the study on the stability and electronic structure of alkali, alkaline-earth and transition metal hydrides. The electronic structures and formation energies of the hydrides are calculated by considering various crystal structures. The hydriding energy was considered to have three contributions. First is the energy required for the transformation of the crystal structure involving atomic rearrangements of the metal atoms upon hydride formation. Second is the energy associated with the expansion of the lattice going from the metallic state to hydride. The third contribution is the chemical bonding between metal atoms and hydrogen. The study [10] showed that the early transition metals have higher tendencies for hydride formation and this tendency was systematically decreased to the right of the periodic table. In a different study, Nagasako et al. [11] investigated C14-type Laves phase Ti–Mn hydrides. Formation energies are expressed in a similar way as Smithson et al. [10]. It is stated that the equilibrium volume and the bulk modulus of the metal are two important parameters in the determination of the formation energy of the hydride. Dompablo and Ceder [12] studied thermodynamic stability of AMH$_4$ and A$_2$MH$_6$ [A = Li, Na, K; M = B, Al, Ga]-type alanate hydrides. It is shown that the overall stability of the hydride and as a consequence temperature and pressure variables of the storage process can be altered by substitution on Na and Al sites. As a result, more hydrogen release may be obtained in a narrower range of temperature and pressure. Hong and Fu [13] investigated the effect of hydrogen on electronic and magnetic properties of ZrX$_2$ (X = V, Cr, Mn, Fe, Co, Ni) Laves phase compounds. The stabilities of the hydrogen at different crystal sites are compared. In a parallel study, Huang et al. [14] inspected the electronic structure and stability of ZrV$_2$ hydrides of different composition. The crystal and electronic structures of all alkali–aluminum and alkali–gallium tetra-hydrides (ABH$_4$; A = Li, Na, K, Rb, Cs; B = Al, Ga) were studied by Vajeeston et al. [15] via projected augmented plane-wave method. It is claimed that BH$_4$ is like a sub-unit in a matrix and an ionic interaction exists between A and BH$_4$ units. Also the strongest bond in the system was defined as B–H bond.

Theoretical methods were also used in the determination of electronic structure for $\beta$ and $\gamma$ phases of FeTi-hydride. Augmented planewave (APW) calculations were done by Gupta [16] for FeTiH. In this study total and partial DOS analysis and bonding characters were presented for $\beta$ phase. Morinaga and friends [17–20] used DV-Xz cluster method in the modeling of several types of binary hydrogen storage alloys. According to Nambu et al. [19], considering two different hydrogen-centered octahedron, the interaction between Fe–H is stronger than Ti–H in FeTiH$_2$. It was also noted that the distortion of lattice during hydrogenation mostly arose among Ti atoms due to relatively weak Ti–Ti bonds. In a recent study of Andreasen [21], a compilation of the literature on theoretical studies of metallic hydrides and their comparison with experimental data is given.

In this study, first principles pseudopotential calculations of FeTiH$_x$ ($x = 1–6$) hydrides are presented. The calculations mainly focused on the subgroups of Pm$\bar{3}$ space group, in which Fe–Ti coordination is similar to the one in Pm$\bar{3}m$. In addition, experimental structures were also considered. The
Table 3
Optimized structural parameters for the stable phases

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Space group</th>
<th>Wyckoff position</th>
<th>Calculated cell parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTi</td>
<td>221</td>
<td>Fe 1a, Ti 1b, H 2c</td>
<td>a 3.011 (2.978), b –, c –</td>
</tr>
<tr>
<td>FeTiH</td>
<td>17</td>
<td>2c 2d, 2a</td>
<td>a 2.978 (2.956), b 4.549 (4.543), c 4.417 (4.388)</td>
</tr>
<tr>
<td>FeTiH2</td>
<td>65</td>
<td>4i 4h, 2a + 2c + 4e</td>
<td>a 7.123 (7.029), b 6.302 (6.233), c 2.819 (2.835)</td>
</tr>
<tr>
<td>FeTiH4</td>
<td>123</td>
<td>1a 1d, 4i</td>
<td>a 2.927, b –, c 4.523</td>
</tr>
</tbody>
</table>

The experimental values are given in parentheses for FeTi, FeTiH and FeTiH$_2$ are due to [2,5,8], respectively.

details of the structural parameters for all structures calculated were given in Table 2. In the reassessment of experimentally derived structures we placed the constituent atoms in Wyckoff positions with the highest site occupancy. The equilibrium states were calculated for every system in Table 2. Relative stabilities of the hydrides are pointed out via formation and mixing energies. Density of states (DOS) are also included in relation with the formation energies and bonding character of the predicted stable hydrides.

2. Computational details

In this study all the computations have been done by the use of the ABINIT code [22] that is based on pseudopotentials and planewaves within density functional theory (DFT). It relies on an efficient fast Fourier transform algorithm [23] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate-gradient method [24] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [25]. We performed generalized gradient approximation (GGA) to DFT. Fritz–Haber–Institute GGA pseudopotentials [26] are used to represent atomic cores. Computational details are as such for the space groups $P2_1/m$ (No. 10), $P222_1$ (No. 17), $Cmmm$ (No. 65), $P4/mmm$ (No. 123), $Pm\bar{3}m$ (No. 200), $P\bar{4}3m$ (No. 215) and $Pm\bar{3}m$ (No. 221) that, an energy cutoff of 22 Hartree and a $12 \times 12 \times 12$ grid for $k$-point sampling was used, for $R\bar{3}m$ (No. 166), 22 Hartree cutoff with a $14 \times 14 \times 14$ grid was used. The unit cells of the structures investigated in this study were constructed using the symmetry and atomic positions as given in Table 2. For example, there are three structures having the $R\bar{3}m$ (No. 166) space group, giving two different compositions. In all these structures Fe and Ti atoms are occupying the 1a and 1b Wyckoff positions, respectively. In the first structure, hydrogen atoms occupy the 2c position in which the obtained hydrogen to metal (H/M) ratio is 1.0. In the second and third structures, hydrogen atoms occupy the 3d and 3e positions, respectively, both yielding the same H/O ratio, which is 1.5. The structures were then fully relaxed in order to obtain the minimum total energy. Although FeTi was found to be non-ferromagnetic [27], we have made spin polarized calculations as well. However, spin polarized
3. Results

3.1. Hydride formation energies

The formation reaction for the FeTi hydride can simply be written as

\[ n \text{FeTi} + H_2 \rightarrow n \text{FeTiH}_2/n. \]  

The coefficients of the reaction are normalized to define the formation energies per one molecule of \( H_2 \) so as to simplify the comparison. \( H_2 \) gas contains an important entropy term however it is not included in first principles calculations. Thus, the energy of \( H_2 \) is approximated to the energy of an \( H_2 \) molecule in vacuum at zero Kelvin. The determined formation energies, therefore, do not represent the absolute values of real formation energies; however, relative energy differences can provide a good means of comparison of systems. Although formation energy is a useful parameter in determination of relative stability, it is sometimes more convenient to use mixing energy for stability comparison between different hydrides i.e. \( \text{FeTiH}_x \) \((x = 1, 2, 3, \ldots)\). Mixing energy is the energy of the reaction, Eq. (2), between two compounds which determines either these compounds mix to form a tertiary compound or phase separation occurs

\[ (1 - x/y) \text{FeTi} + x/y \text{FeTiH}_y \rightarrow \text{FeTiH}_x. \]  

In Fig. 1(a) and (b), respectively, the calculated formation energies per mole of \( H_2 \) and mixing energies per mole of the formed hydride were given. Each point in these figures represents the calculated energy value of a different crystal structure at that given hydrogen composition (see Table 2). The tie lines in Fig. 1(b), forming the smallest convex around the points, trace the lowest energy path between phases. These in turn visualize a simple phase distribution diagram.

When only the hydrogen compositions are considered, the calculations indicate that only mono and di-hydrides are stable since only for these compositions negative formation energies were obtained. In addition, for the tetra-hydride composition a nearly stable structure was identified. When the crystal structures are considered, the most negative formation energy among mono-hydrides has the orthorhombic structure \((P222_1)\), which was the experimental structure of FeTiH according to Thompson et al. [5] and Fischer et al. [28]. Similarly, the experimentally found structure \((Cmmm)\) of the di-hydride due to Thompson et al. [6] and Fischer et al. [8], also became the lowest-energy system in our calculations. Formation
energies of FeTiH and FeTiH₂, at zero Kelvin, were found to be 21.9 and 15.5 kJ per mol of H₂, respectively. The experimentally determined heat of formation of FeTiH₂ was given as 28.1 kJ/mol (at \( P = 5.2 \text{ atm} \) and \( T = 303 \text{ K} \)) and 26.7 kJ/mol (at \( P = 11 \text{ atm} \) and \( T = 324 \text{ K} \)) in hydride information center [29]. The computed lattice parameters for these structures came out to be very close to the experimental values, see Table 3, errors being in the order of 1%–1.5% which is acceptable for the DFT approximation.

In mono-hydride (\( P222_1 \)), the hydrogen is located inside an octahedral site surrounded with four titanium and two iron atoms, Fig. 2(a). However, in di-hydride (\( Cmmm \)), there are two kinds of octahedral hydrogen sites one having a similar coordination with FeTiH and one caged by four iron and two titanium atoms, Fig. 2(b). Crystal systems having negative formation energies other than \( P222_1 \) and \( Cmmm \), have also hydrogen at octahedral interstitial sites as in Fig. 2(a). All structures, containing 2Fe–4Ti octahedron, have bond lengths of Fe–H 1.7–1.8 Å, Ti–H 2.1–2.2 Å. As a general trend, systems having Fe–H bond length smaller than that of Ti–H have relatively lower energies. Smaller bond length indicates stronger interaction between iron and hydrogen in the structure.

At FeTiH₄ composition the calculated lowest-energy structure has a different metallic coordination around hydrogen. Rather than having an octahedral cage as in previously discussed stable structures, hydrogen has a tetrahedral coordination of two iron and two titanium atoms, Fig. 3. The calculations also showed that for the FeTiH₃, structures with H in octahedral cages are not the lowest-energy states. Close inspection of Fig. 2 reveals that, the octahedral framework of FeTiH is conserved when FeTiH₂ is produced. New hydrogen atoms are positioned at the other octahedral site of the structure without altering the previous one. Due to this structure preservation, the transformation reaction from mono to di-hydride has an energy bonus. On the other hand, the octahedral framework is destroyed when FeTiH₄ is formed, see Fig. 3. This in turn necessitates extra energy. The increase in the formation energy for FeTiH₄ can easily be correlated to this condition. Positive formation energy of this compound indicates that it is unstable. However, the magnitude is very small (∼3.5 kJ/mol H₂). A minor decrease, therefore, can favor the formation of this compound. Moreover, a small negative formation energy is advantageous when desorption is considered. So, with appropriate alterations in the composition of the intermetallic phase or temperature and pressure of the storage system, the tetra-hydride may be obtained.

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>FeTi</th>
<th>FeTiH</th>
<th>Differential charge</th>
<th>FeTiH₂</th>
<th>Differential charge</th>
<th>FeTiH₃</th>
<th>Differential charge</th>
<th>FeTiH₄</th>
<th>Differential charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total charge</td>
<td>Total charge</td>
<td></td>
<td>Total charge</td>
<td>Differential charge</td>
<td>Total charge</td>
<td>Differential charge</td>
<td>Total charge</td>
<td>Differential charge</td>
</tr>
<tr>
<td>Fe</td>
<td>6.3024</td>
<td>6.391</td>
<td>0.0960</td>
<td>6.4083</td>
<td>0.1721</td>
<td>6.4331</td>
<td>0.3501</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1.9102</td>
<td>1.8992</td>
<td>0.0506</td>
<td>1.9359</td>
<td>0.1333</td>
<td>1.9524</td>
<td>0.2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>1.2825</td>
<td>0.7121</td>
<td>1.1560</td>
<td>0.56296</td>
<td>1.2771</td>
<td>0.7505</td>
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</tr>
<tr>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.2620</td>
<td>0.7071</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–</td>
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<td>–</td>
<td>1.2657</td>
<td>0.6245</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Valence charges for isolated Fe, Ti, and H are 8, 4, and 1, respectively.
3.2. Electronic structure of the hydrides

The electronic DOS for FeTi are given in Fig. 4. The Fermi energy is normalized to zero and will be so for the rest of the figures. A partial DOS analysis into its angular momentum components shows that $3d$ contribution dominates for both Fe and Ti in accordance with literature. Papaconstantopoulos [27] states that below Fermi level main contributor is iron, while titanium dominates above Fermi energy. According to our calculations, iron is the main contributor at bonding manifold as in Papaconstantopoulos [27] study, however, iron also contributes the anti-bonding states but not as much as in bonding. In addition, the decomposed $d$ state densities are similar over the same energy distribution, thus the $3d$ orbital hybridization is primary.

Calculations show very similar total and partial DOS structures for FeTiH with Gupta [16], which are given in Fig. 5. Position of Fermi energy indicates that the hydride has a metallic character. The low-energy states can principally be identified as hydrogen $1s$ state. These manifestations at low energy are basically due to hydrogen $s$ and to a lesser extent metal $d$ state. Below Fermi level, Fe $3d$ governs the total DOS as Ti $3d$ dominates above.

In order to have a better picture of changes following hydrogen insertion to the system, the structure of FeTiH ($P2\overline{2}2_1$) without hydrogen, was electronically relaxed keeping the cell shape and size constant as that of structurally relaxed FeTiH. DOS of the FeTiH and FeTi in $P2\overline{2}2_1$ space group and the difference in their charge densities (differential charge density) are plotted in Fig. 6(a and b). The examination of state densities shows an increase in the anti-bonding states and an expansion of DOS through higher energies above Fermi level as hydrogen is inserted. This is especially apparent in the partial DOS of titanium, as seen from Figs. 5 and 6(a). This is due to the charge transfer from metals to hydrogen. When iron and titanium states are compared with their no hydrogen condition, it is seen that titanium is the main donor rather than iron.
The integration of charge density inside the spheres around iron and titanium in FeTi, Table 4, shows that more electrons are dispersed throughout the structure from Ti when compared to Fe. This is consistent with the electronegativity values of constituent atoms. Hirshfeld [30] charge analysis reveals that Ti gained a net charge of 0.0232 and Fe lost 0.0232 during the formation of FeTi. This confusing result is due to the fact that Hirshfeld analysis accounts the dispersed charged in favor of Ti since the electronic density of the isolated Ti becomes higher than Fe at distant points.

It is seen from the charge density data of FeTiH, Fig. 6(b) and Table 4, that the total charge on the hydrogen is more than one, that is, hydrogen has attracted some of dispersed electrons. Moreover, a very small amount of differential charge is accumulated inside the spheres of iron and titanium. This might be due to the beginning of charge localization on atoms because of a change in metallic character of the bonds. Electron interaction between iron and hydrogen appears to be the strongest of all which is in accordance with the previous studies [18,20]. For iron, the charge increased at $d$ orbitals which are aligned towards the hydrogen, whereas it is decreased at the $d$ orbitals that are not pointing the hydrogen atoms, Fig. 6(b).

Electronic trends are similar in FeTiH$_2$ (Cmmm) structure, see Fig. 7. In addition, more charge is accumulated on iron and titanium which may imply an increase in the electron localization, see Table 4. When iron orbitals are observed, the charge is again collected at $d$ orbitals which are aligned towards hydrogen and vice versa for non-aligned ones, Fig. 8(b).

The DOS analysis of FeTiH$_4$, Fig. 9, produces similar results with previous compounds in bonding and anti-bonding character of constituent atom states. The number and energy of hydrogen states are progressively increased with increasing hydrogen content from FeTiH to FeTiH$_4$. The localization of charge still continues on metal atoms, see Table 4. On the other hand, the analysis of charge density difference plot for FeTiH$_4$ shows a different condition for the charge distribution around iron, see Fig. 10(b). Unlike mono and di-hydride, for FeTiH$_4$, charge is collected at orbitals which are not aligned towards the hydrogen and depletion of electrons occurs at orbitals that are pointing the hydrogen.
4. Conclusions

We have investigated stoichiometric FeTi hydride system up to \( H/M = 3 \) i.e. \( \text{FeTiH}_6 \), by using first principles DFT in GGA approach. Ab initio results are in agreement with experimentally determined ground states for \( \text{FeTiH} \) and \( \text{FeTiH}_2 \). From our calculations we have predicted the formability of a higher \( H \) content structure, \( \text{FeTiH}_4 \). Although it seems not to be stable, it is nearly stable or can be made stable with some chemical make up. It is also found that storing more \( H \) above \( H/M = 2 \) into FeTi chemistry seems to be unlikely.

The primary octahedral framework of \( \text{FeTiH} \) is conserved when \( \text{FeTiH} \) is transformed into \( \text{FeTiH}_2 \) and hydrogen additions produce a second kind of octahedral site. However, this octahedral metal organization around \( H \) has changed to tetrahedral framework for \( \text{FeTiH}_4 \), causing an increase in formation energy of this compound.

DOS analysis shows that bonding manifold is dominated by hydrogen 1s and iron 3d states; on the contrary, antibonding states are mainly titanium 3d for hydrides. The increase in the antibonding states, especially in Ti, indicates the charge transfer to hydrogen. Computations also revealed that in ground states of mono and di-hydride, electrons around iron, are collected at preferred orbitals which are aligned towards hydrogen and the ones that are not pointing hydrogen are depleted. The exact opposite situation exists for \( \text{FeTiH}_4 \).

Acknowledgments

The numerical calculations reported in this paper were carried out at the ULAKBIM High Performance Computing Center at the Turkish Scientific and Technical Research Council (TUBITAK).

References