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First-Principles Calculations of Hydrogen Insertion Effects on Electronic Properties of $TiCr_2$ and $Ti_{0.875}Mg_{0.125}Cr_2$

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Abstract

$TiCr_2$ based alloys of AB_2 type with C_{15} Laves phase structure are good candidates for hydrogen storage. In this work, we used density functional theory and plane-wave pseudo potential technique to study electronic properties of $TiCr_2H_3$ and $TiMgCr_2H_3$. In $TiCr_2$, the H atom interacts more strongly with the Ti than with Cr atoms and tends to occupy the g (2A2B) site; the $TiCr_2H_3$ has an insulating character. In $Ti_{0.875}Mg_{0.125}Cr_2H_3$, H atoms interact with both Ti atom and Mg atom, and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ conserves its metallic character. Structural stability of $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ is investigated by calculating their formation enthalpies. Total and partial electronic densities of states and electronic charge differences of the compounds are also computed and discussed.

Keywords: Laves phases; Hydrogen storage; DFT

Introduction

Hydrogen as a vast fuel source has attracted tremendous attention over the years. As a key part of the hydrogen-energy utilization, how to store hydrogen efficiently is still a challenging problem for us until now [1-5]. Developing safe, cost effective, and practical means for storing hydrogen is crucial to the advancement of hydrogen-energy and fuel-cell technologies. Compared with other technologies like gas compression or liquefaction, solid-state materials such as metal alloys can store hydrogen at relatively low pressure and ambient temperatures [6-9]. Moreover, the volumetric densities of hydrogen storage for some metal hydrides even exceed that of solid H_2 [10]. Therefore, metal hydrides are of major interest for hydrogen storage and have been extensively investigated. $TiCr_2$ is one of the most abundant intermetallic compounds which it still attract attention and interest of researchers [11-15] since it has a great potential for high temperature structural applications and hydrogen storage. Compared with other technologies of hydrogen storage, such as gas compression or

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liquefaction, solid-state materials such as metal alloys can store hydrogen at ambient temperatures and relatively low pressure. Thus, metal hydrides are very interesting for hydrogen storage and have been extensively investigated. However, $TiCr_2$ compound has not been largely commercialized in view of the fact that it is very brittle at low temperature and has a high density. This paper, reviews the important effect of insertion hydrogen in $TiCr_2$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$. Both compounds are taken in cubic phase named C_{15} which is the more stable for hydrogenated compounds [16]. Firstly, the stabilities of the binary compound and its alloy are examined by calculating the enthalpies of formation and then their structural properties are investigated. Each structure was optimized by full relaxation and the lattice parameters are obtained. Electronics properties are also studied and densities of states of C_{15}-$TiCr_2H_3$ and of C_{15}-$TiMgCr_2H_3$ have been calculated and discussed.

Materials and Methods

Computational details

First-principles calculations were performed using density functional theory DFT [17] and plane-wave pseudo potential technique, as implemented in the VASP code [18]. For correlation interaction, we used the projector-augmented wave (PAW) method [19,20], the set of valence states include 3d3 4s1 and 3d5 4s1 for Ti and Cr respectively, whereas the electron configuration for Mg treats 3s2 states as valence state. An over energy of cut-off of 400 eV is considered for all calculations performed in this study. The exchange and correlation energy is treated within generalized gradient approximation (GGA) of Perdew-Wang (PW91) [21].

The Brillouin-zone integrations used Monkhorst-Pack grids [22] with a mesh of 11 × 11 × 11, (Γ point centered) for both compounds.

Results and Discussion

Structural properties and stability of $TiCr_2H_3$ and $TiMgCr_2H_3$

The C_{15}-$TiCr_2$ intermetallic compound is face-centered cubic lattice with $Fd\bar{3}m$ space group N° 227. It closes two AB2 formula units per unit cell. The Ti atoms are considered as A-type and Cr atoms as B-type. In such structure, specific environment is depicted by A and B-type atoms. A diamond like sub lattice is formed by A-type atoms, and in the interstitial space of the A-type sub lattice, B-type atoms form tetrahedrons. From our calculations, the equilibrium lattice constant for the $TiCr_2$ crystal is 6.857 Å, which compares well with the experimental value of 6.910 Å [23] or 6.932 Å [24]. For $Ti_{0.875}Mg_{0.125}Cr_2$ alloy, the calculated equilibrium lattice constant is 7.02 Å. Regarding the hydrogen insertion in the AB2 compound, H atoms can occupy only specific sites i.e., 8b, 32e, and 96g as defined by the Wyckoff positions. These positions correspond to the tetrahedral interstitial sites 4B site, 1A3B site, and 2A2B site respectively [25-27]. We compare the incorporation of the H atom in these three interstitial sites by computing the absorption energy. The results are listed in TABLE 1. For the most favorable g site, the absorption energy for a single H atom within $TiCr_2$ lattice is -0.29 and within $Ti_{0.875}Mg_{0.125}Cr_2$ it is equal to -0.25.

TABLE 1. **Absorption energies of H atom in three kinds of interstitial site in both $TiCr_2$ and $Ti_{0.875}Mg_{0.125}Cr_2$ compounds.**

Compounds	**Sites**		
	b (4B)	**e (1A3B)**	**g (2A2B)**
$TiCr_2$	1.92	-0.08	-0.29
$Ti_{0.875}Mg_{0}.125Cr_2$	1.04	-0.02	-0.25

In order to investigate the stability of the hydrogenated compounds $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$, their enthalpies of formation ΔH are calculates using the total energies. The reaction related to the decomposition of the hydride $TiCr_2H_3$ and the release hydrogen is: $TiCr_2H_3 \rightarrow TiCr_2H+H_2$. Therefore, the enthalpy of formation is calculated by the subtraction of the total energies of $TiCr_2H$, and of the hydrogen molecule from the hydride $TiCr_2H_3$.

ΔH is given by:

$$\Delta HTiCr_2H_3=(TiCr_2H_3) - Etot\ (TiCr_2H) - Etot\ (H_2) \qquad (1)$$

And for $Ti_{0.875}Mg_{0.125}Cr_2H_3$, ΔH is given by:

$$\Delta HTiMgCr_2H_3=(TiMgCr_2H_3) - Etot\ (TiMgCr_2H) - E(H_2) \qquad (2)$$

The total energies of $TiCr_2H_3$, $TiCr_2H$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$, $Ti_{0.875}Mg_{0.125}Cr_2H$ are calculated when structures are optimized and relaxed, while the energy of H_2 has been calculated for an isolated molecule in a repeating cube and only the H-H bond length was allowed to relax. With the cube of 6 Å of edge length the calculated energy is 31.7012 eV. The total energies of $TiCr_2H$ and of $TiMgCr_2H$ are respectively -38.0016 eV and -27.3812 eV.

TABLE 2. **Lattice parameters a, total energies E and formation enthalpies ΔH of $TiCr_2$, $Ti_{0\cdot875}Mg_{0.125}Cr_2$, $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$.**

Compounds	**Lattice parameters a**	**Total energies E**	**Formation enthalpies ΔH**	
	(Å)	**(eV)**	**(eV/atom)**	**$kJ\cdot mol^{-1}$ H**
$TiCr_2$	6.857	-39.808	-0.121	-
$TiCr_2H_3$	6.98	-69.7278	-0.16	-15.401
$Ti_{0.875}Mg_{0.125}Cr_2$	6.84	-30.3705	-0.117	-
$Ti_{0.875}Mg_{0.125}Cr_2H_3$	7.02	-60.2318	-0.834	-80.25

We can see from TABLE 2 that the lattice parameter of TiCr2H3 is larger than that of $TiCr_2$. The same observation is valid for $Ti_{0.875}Mg_{0.125}Cr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2$. We deduce that for both $TiCr_2$ and $Ti_{0.875}Mg_{0.125}Cr_2$, lattice parameters increase when hydrogen is incorporated. Others works found the same result for $TiCr_2$ with different concentration of H where the expansion of volume is specified when H enhances from 0 to 7.

Total and partial electronic densities of states of $TiCr_2H_3$

To examine the important effect of insertion hydrogen on electronic properties, total and partial densities of states of $TiCr_2H_3$ are computed and are represented in FIG. 1. One can see that the presence of hydrogen atoms within the $TiCr_2$ introduces some s bands in the low-energy region from -4.5 eV to 0 eV. This modifies remarkably the electronic states around the Fermi level, and an electronic gap of about 1 eV is created. The compound adopts an insulating character due to the presence of holes. The hydrogen acts as acceptor and the $TiCr_2H_3$ is a semiconductor.

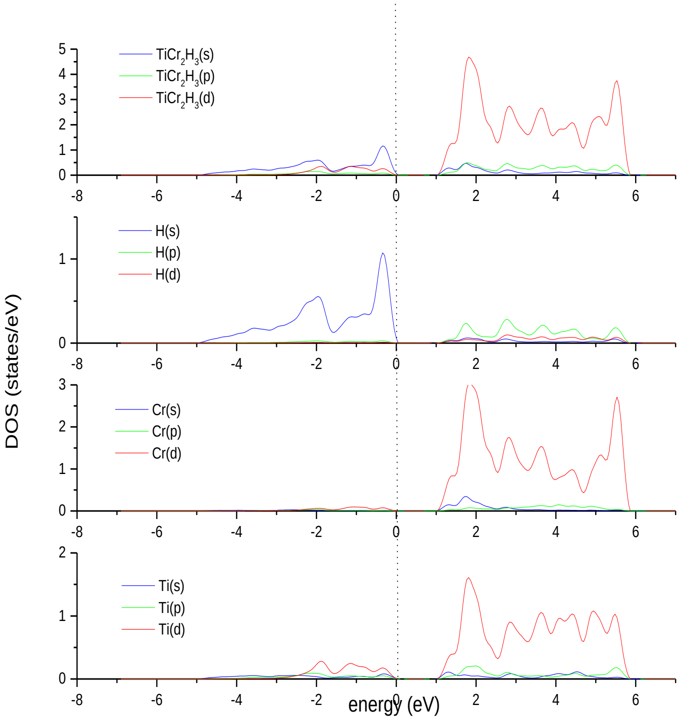

FIG. 1. **Electronic densities of states of $TiCr_2H_3$.**

The s bands associated to H atoms have two main peaks at -0.40 eV and -1.97 eV. The s states around the two peaks have moderate hybridization with the d-Ti states. This hybridization reflects the hydrogen-metal interaction and suggests that H atoms interact strongly with the hydride formation element Ti (A type) rather than with the hydride non-formation element Cr (B type).

The metallic character of $Ti_{0.875}Mg_{0.125}Cr_2$ is retained for the $Ti_{0.875}Mg_{0.125}Cr_2H_3$ compound, and the electron excess is shared between H and Mg atoms. The conduction band is occupied substantially by the d-Ti states and a small contribution comes from d-Cr and s-Mg, p-Mg states.

Total and partial electronic densities of states of $Ti_{0.875}Mg_{0.125}Cr_2H_3$

FIG. 2 shows the total and the partial densities of states of $Ti_{0.875}Mg_{0.125}Cr_2H_3$. It can be seen that absorption of hydrogen atoms within the $Ti_{0.875}Mg_{0.125}Cr_2$ lattice introduces some s bands in the low-energy region between -6 eV and -3 eV. Under -4 eV, deepest hybridizations are between s-H states and s-Mg states and between s-H states and d-Ti states. From -3.5 eV to -2.5 eV the hybridization is between s-H states, d-Ti states and p-Mg states, and from -2 eV to Fermi level it is between d-Ti states and d-Cr states. A careful examination of the 3d bands of Cr and Ti shows that they are modified due to the presence of Mg. In $Ti_{0.875}Mg_{0.125}Cr_2H_3$, H atoms interact strongly with the hydride formation element Ti (A type) and with Mg rather than with the hydride non-formation element Cr (B type).

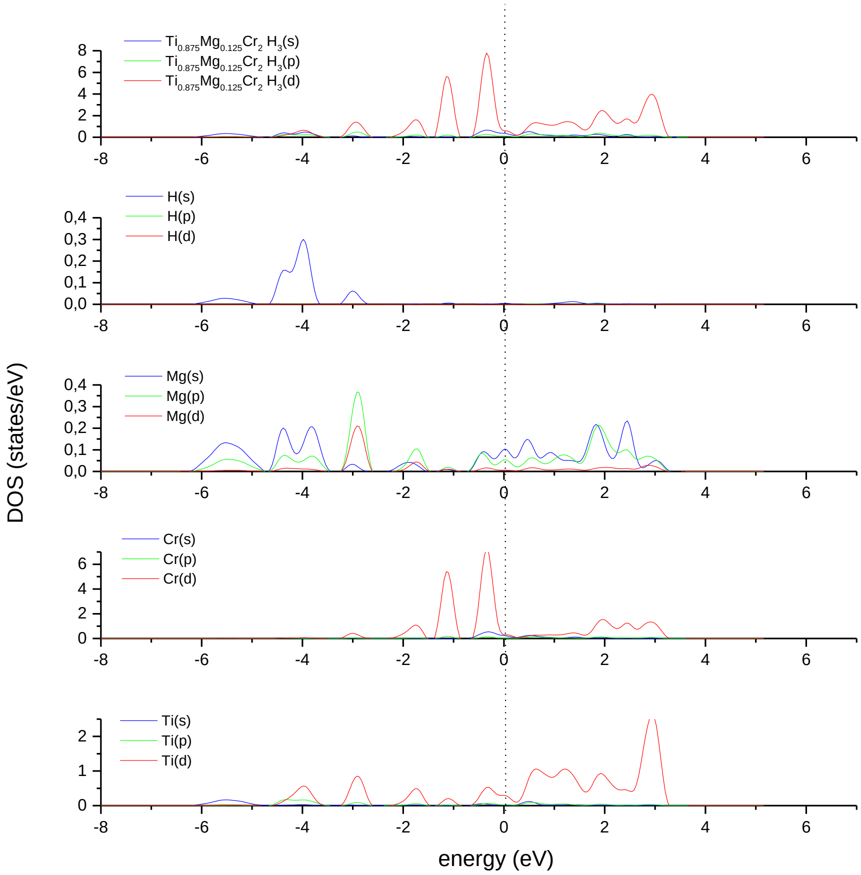

FIG. 2. **Electronic densities of states of $Ti_{0.875}Mg_{0.125}Cr_2H_3$**

The metallic character of $Ti_{0.875}Mg_{0.125}Cr_2$ is retained for the $Ti_{0.875}Mg_{0.125}Cr_2H_3$ compound, and the electron excess is shared between H and Mg atoms. The conduction band is occupied substantially by the d-Ti states and a small contribution comes from d-Cr and s-Mg, p-Mg states.

Electronic charge densities difference of $TiMgCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$

In order to examine the interaction between Cr, Ti, Mg and H atoms, we plot the valence electron charge densities difference of $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ in FIG. 3. (a). The valence electron charge density difference $\Delta\rho$ is given by:

$\Delta\rho=\rho TiCr_2H_3 -\rho H3$……………………………….for $TiCr_2H_3$ compound.

$\Delta\rho=\rho Ti0.875Mg0.125Cr_2H_3-\rho Mg-\rho H3$…………for $Ti_{0\cdot875}Mg_{0\cdot125}Cr_2H_3$ compound.

Where $\rho TiCr_2H_3$and $\rho Ti_{0.875}Mg_{0.125}Cr_22H_3$ are the valence charge density of $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ compounds, ρMg and $\rho H3$ are calculated for isolated Mg and H of the same super cell, respectively.

One can see from FIG. (3a) of charge density difference of $TiCr_2H_3$, that there is a deepest charge transfer from Ti to H atom which reflects the interaction between Ti and H atoms. H atoms react more with Ti than with Cr atom.

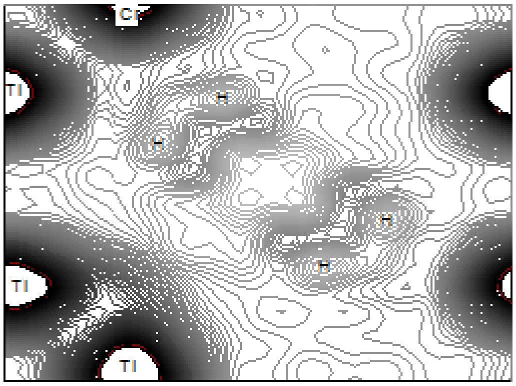

FIG. 3(a). **Electronic charge densities difference of $TiCr_2H_3$.**

From FIG. 3(b) of charge density difference of $Ti_{0.875}Mg_{0.125}Cr_2H_3$, we notice that between H and Mg atom, the bond is ionic since the charge is concentrated at atoms. Moreover H atom reacts more with Ti and Mg than with Cr atom. The small charge shift between the Ti, Mg and H atoms reflects the interaction between Ti-H and between Mg-H atoms. In this case, the compound conserves its metallic character. In both $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ compounds, a charge accumulation between Ti and Cr atom is characteristic of polar covalent bond between Ti and Cr.

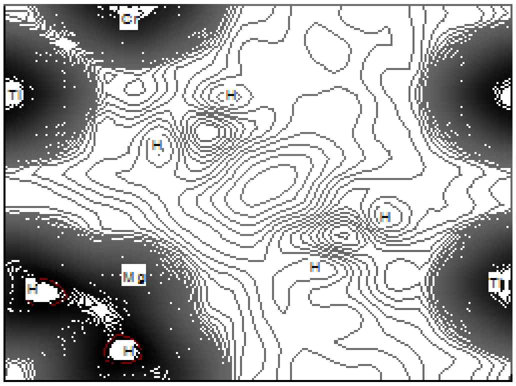

FIG. 3(b). **Electronic charge densities of $Ti0.876Mg_{0.123}Cr_2H_3$.**

Conclusion

We have carried out first-principles calculations for the $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$. The absorption energies of the H atoms at different interstitial sites show that the hydrogen atoms tend to occupy the g interstitial sites. The result of enthalpies of formation of $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ shows that both compounds are stables and the hydrogenation of $TiCr_2$ and $Ti_{0.875}Mg_{0.125}Cr_2$ is feasible and favorable. For the host compound $TiCr_2$ lattice parameter expands when hydrogen is added to. The same result is found for $Ti_{0.875}Mg_{0.125}Cr_2$. The examination of the electronic densities of states of $TiCr_2H_3$ and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ suggest that in the first hydride, H atoms interact stronger with the hydride formation element Ti (A type) rather than with the hydride non-formation element Cr (B type), and $TiCr_2H_3$ has an insulating character. In the second hydride, H atoms interact stronger with both the hydride formation element Ti (A type) and with Mg than with the hydride non-formation element Cr (B type) and $Ti_{0.875}Mg_{0.125}Cr_2H_3$ conserves its metallic character.

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