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Fundamental mechanism of tetragonal transitions in titanium hydride

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ABSTRACT

First principles calculation reveals that the tetragonal transitions of TiH_x ($1 \le x \le 2$) could be divided into two types in terms of energy pathway, and that the intrinsic composition range of the $\delta \rightarrow \varepsilon$ transition is $1.5 \le x \le 2$. Calculation also indicates that the fundamental reasons for the $\delta \rightarrow \varepsilon$ and $\delta \rightarrow \gamma$ transitions are quite different from each other, i.e., mechanical instability causes the $\delta \rightarrow \varepsilon$ transition and internal symmetry breaking of cubic structures induces the $\delta \rightarrow \gamma$ transition. In addition, the Poisson ratio of δ phases between the x and z axes is proposed to provide a deeper understanding of intrinsic natures of tetragonal transitions.

1. Introduction

Titanium hydrides are regarded as important phases in Ti alloys designed for hydrogen storage and various structural applications [1]. It is well known that TiH_x ($1 \le x \le 2$) has tetragonal transitions from the FCC structure (δ phase) to two face-centered-tetragonal (FCT) structures ($c/a < 1$, ε phase; $c/a > 1$, γ phase) [2]. The starting compositions of the $\delta \rightarrow \varepsilon$ transition, however, are quite different from experiments in the literature, i.e., $x = 1.70$ [3], $x = 1.73$ [4], $x = 1.77$ [5], $x = 1.85$ [6], $x = 1.90$ [7], and $x = 1.924$ [8]. Fundamentally, an intrinsic composition range for the $\delta \rightarrow \varepsilon$ transition should exist and have nothing to do with experimental techniques. Another controversy about tetragonal transitions is that for $TiH_{1.75}$ and TiH_2, both $\delta \rightarrow \varepsilon$ and $\delta \rightarrow \gamma$ transitions were observed from theoretical calculations, while only the $\delta \rightarrow \varepsilon$ transition was confirmed experimentally [9–11]. In addition, the underlying reason for the $\delta \rightarrow \varepsilon$ transition has been investigated extensively [9–13], whereas the mechanism of the $\delta \rightarrow \gamma$ transition is still unrevealed, as more attention was paid to the stability of γ phase as well as $\alpha \rightarrow \gamma$ transition [14–17]. In this study, first principles calculations are conducted to clarify the above controversies in the literature, and to reveal the fundamental mechanism of tetragonal transitions in TiH_x.

2. Calculation methods

The calculation is based on the well-established Vienna ab initio simulation package with the projector-augmented wave method and generalized gradient approximation [18,19]. Accordingly, five compositions of TiH_x are selected for the δ structure, i.e., an FCC unit of 4 Ti atoms with the additions of 4, 5, 6, 7, and 8H atoms stand for TiH, $TiH_{1.25}$, $TiH_{1.5}$, $TiH_{1.75}$, and TiH_2 phases, respectively. To derive the FCT structures, the original c/a ratio of 1 for each FCC TiH_x is changed from 0.80 to 1.20 with an interval of 0.01, in order to identify the two local minima of total energy corresponding to the γ ($c/a > 1$) and ε ($c/a < 1$) phases. At each c/a ratio, the volume and atomic positions are fully relaxed, while the crystal shape is kept constant. The cutoff energies are 450 eV for plane-wave basis, and the k-meshes of $15 \times 15 \times 15$ and $21 \times 21 \times 21$ in corresponding reciprocal lattice ($2\pi/a$, $2\pi/a$, $2\pi/c$) of each structure are selected for relaxation and static calculations, respectively. It should be pointed out that the H atoms are located at the tetrahedral interstitial sites of the lattice, and the combination of letters (a–h) is used to express the atomic configuration of H, i.e., the energetically preferable configurations of (*abgh*) and (*abceg*) for TiH and $TiH_{1.25}$, respectively; three configurations of (C_1:*abcfgh*), (C_2:*abcdeg*), and (C_3:*abcdef*) for $TiH_{1.5}$; and only one H configuration for $TiH_{1.75}$ and TiH_2 [20].

3. Results and discussion

After the calculation, it could be seen that the derived properties of various TiH_x phases are in good agreement with available experimental results in the literature [3,5,21–23]. For instance, the present lattice constants of ε $TiH_{1.75}$ are $a = 4.467$ Å and $c = 4.244$ Å, which are consistent with corresponding experimental values of $a = 4.475$ Å and $c = 4.372$ Å [5]. The heat of formation (-160.15 kJ/mol·Ti) of δ TiH_2 also matches well with the standard δH_f at 0 K (-165 kJ/mol·Ti) [23].

To locate the FCT structures, the total energies as a function of c/a ratio are calculated and derived for each TiH_x phase. As a

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typical example, Fig. 1 shows the energy curves of $TiH_{1.5}$ with H configurations of C_1, C_2, and C_3. It could be seen clearly that the tetragonal transitions of $TiH_{1.5}$ would be divided into two types in terms of energy pathway, i.e., type I for both C_2 and C_3 with only one energy minimum corresponding to the $\delta \rightarrow \gamma$ transition, and type II for C_1 with two minima corresponding to the $\delta \rightarrow \varepsilon$ and $\delta \rightarrow \gamma$ transitions. Furthermore, the present results also indicate that the tetragonal transitions of TiH and $TiH_{1.25}$ belong to type I, while the energy curves of $TiH_{1.75}$ and TiH_2 are regarded as type II (figures not shown). It should be pointed out that such a classification of tetragonal transitions is proposed for the first time in the present study, and that the two energy minima of type II for $TiH_{1.5}$, $TiH_{1.75}$, and TiH_2 agree well with other theoretical prediction in the literature [9–11].

We now investigate the characteristics of the tetragonal transition of type II for $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2 phases. Accordingly, the atomic volume of TiH_2 as a function of c/a ratio is displayed in Fig. 2 as a typical example. It could be seen that the atomic volume reaches the highest point when c/a equals 1.0 (δ structure), and that there is an almost linear decrease of atomic volume with the decrease or increase of c/a from 1.0 (ε or γ structures). Moreover, the absolute values of the slopes of volume curve as a function of c/a are calculated to be 8.68, 7.55, and 7.68 $Å^3/(c/a)$ for the $\delta \rightarrow \varepsilon$ transitions of $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2, respectively, which are much bigger than the corresponding values of 4.19, 3.69, and 4.09 $Å^3/(c/a)$ for the $\delta \rightarrow \gamma$ transitions. Considering that the coefficients of linear thermal expansion of TiH_x are very big values of about 2.0×10^{-5} /K [24] and the tetragonal transition is the second-order phase transition, such a huge difference of volume contraction between $\delta \rightarrow \varepsilon$ and $\delta \rightarrow \gamma$ with the decrease of the temperature implies that the $\delta \rightarrow \varepsilon$ transition would be far more likely to happen preferentially, and the $\delta \rightarrow \gamma$ transition would be thus impeded by $\delta \rightarrow \varepsilon$, although the energy difference between ε and γ is very small [9–11]. This would therefore give a reasonable explanation to the above-mentioned controversy that both $\delta \rightarrow \varepsilon$ and $\delta \rightarrow \gamma$ transitions of $TiH_{1.75}$, and TiH_2 were observed from theoretical calculations, while only the $\delta \rightarrow \varepsilon$ transition was confirmed experimentally [9–11].

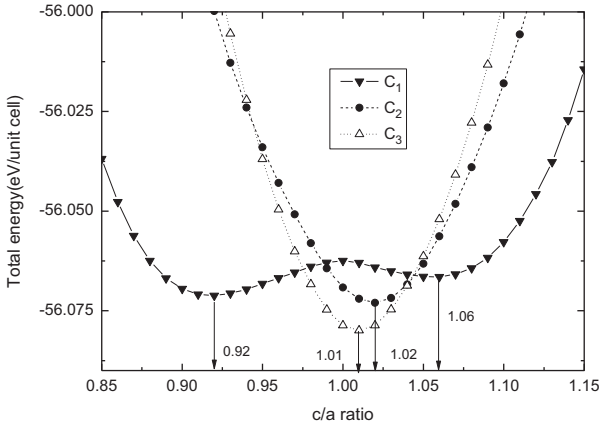

Fig. 1. Total energies of $TiH_{1.5}$ with H configurations of C_1, C_2, and C_3.

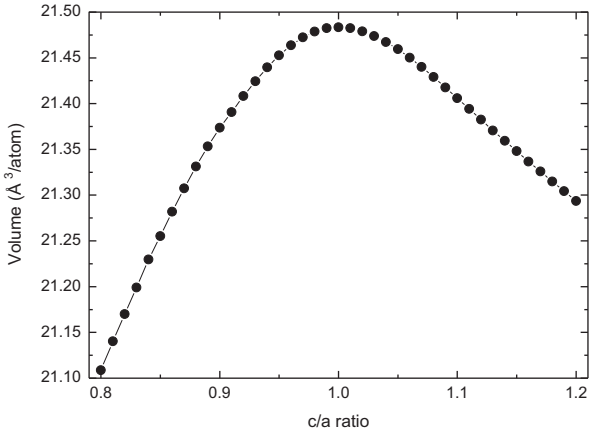

Fig. 2. Atomic volume of TiH_2 as a function of c/a ratio.

It is of interest to reveal the composition range for the $\delta \rightarrow \varepsilon$ transition at the ground state of 0 K. The above calculated results signify that the $\delta \rightarrow \gamma$ transition (type I) is found in TiH, $TiH_{1.25}$, and $TiH_{1.5}$ (C_2 and C_3) phases, while the $\delta \rightarrow \varepsilon$ transition (type II) is discovered in $TiH_{1.75}$, TiH_2, and $TiH_{1.5}$ (C_1). That is to say, both $\delta \rightarrow \gamma$ and $\delta \rightarrow \varepsilon$ transitions could happen only in the $TiH_{1.5}$ phase, and a transfer of tetragonal transition from $\delta \rightarrow \gamma$ to $\delta \rightarrow \varepsilon$ takes place just at $TiH_{1.5}$, suggesting that the present composition range of the $\delta \rightarrow \varepsilon$ transition in TiH_x would be $1.5 \leq x \leq 2$. It should be noted that the experimentally obtained starting compositions ($x=1.70$ [3], $x=1.73$ [4], $x=1.77$ [5], $x=1.85$ [6], $x=1.90$ [7], and $x=1.924$ [8]) are all within the present composition range. Such a nice agreement could not only bring about reasonable clarification to the above-related experimental controversy, but also imply that the present derived composition should be an intrinsic range independent of experimental techniques.

Regarding the underlying mechanism of the $\delta \rightarrow \varepsilon$ transition in TiH_x, there are already several different interpretations in the literature, i.e., splitting of the degenerate bands at E_f along $\Gamma - L$ direction by means of the Jahn–Teller effect [9,10,12], the reduction of the density of states at E_f in the $\Gamma - K$ direction [12], and the Van Hove singularity [10]. In the present study, the shear moduli of the {110} planes at 0 K, i.e., $(C_{11} - C_{12})/2$, are calculated to be -29, -16, and -62 GPa for δ $TiH_{1.5}$(C_1), $TiH_{1.75}$, and TiH_2 phases, respectively. Such negative values of $(C_{11} - C_{12})/2$ suggest that the δ structures of $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2 should be mechanically unstable at 0 K according to the strain energy theory, and that the {110} $< 110 >$ shear would happen spontaneously to induce the $\delta \rightarrow \varepsilon$ transition. It should be noted that after the tetragonal transition, the ε structures (FCT) of $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2 are all mechanically stable. In other words, it is mechanical instability which fundamentally leads to the $\delta \rightarrow \varepsilon$ transition of TiH_x phases.

It is of importance to further find out the fundamental mechanism of the $\delta \rightarrow \gamma$ transition in TiH_x. First of all, the present calculation shows that the δ TiH, $TiH_{1.25}$, and $TiH_{1.5}$ (C_2 and C_3) phases are all mechanically stable with positive values of $(C_{11}-C_{12})/2$, which seem rather dissimilar from the δ $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2 phases with mechanical instability related before. Such a feature of δ structure implies that the $\delta \rightarrow \gamma$ transition in TiH_x phases should not be triggered by mechanical instability. Second, the electronic structures of the δ TiH, $TiH_{1.25}$, and $TiH_{1.5}$ (C_2 and C_3) phases are also quite different from those of δ $TiH_{1.5}$ (C_1), $TiH_{1.75}$, and TiH_2. As shown in Fig. 3, the degenerate bands of δ $TiH_{1.75}$ and TiH_2 around Fermi level (E_f) bring about the high density of states (DOSs) at E_f and Jahn–Teller instability [9,10,12], which consequently induce the $\delta \rightarrow \varepsilon$ transition with degenerate bands split and lower DOSs at E_f. On the contrary, it could be seen clearly from Fig. 3 that the split of degenerate bands has already happened in the δ structures of TiH(*abgh*), $TiH_{1.25}$(*abceg*), and $TiH_{1.5}$ (C_3), and that the $\delta \rightarrow \gamma$ transition has much less effect on electronic structure than the $\delta \rightarrow \varepsilon$ transition. That is the fundamental reason why the δ TiH, $TiH_{1.25}$, and $TiH_{1.5}$ (C_2 and C_3) phases are mechanically stable as shown before. Therefore, it can be deduced that both mechanical instability and Jahn–Teller effect in the $\delta \rightarrow \varepsilon$ transition [9,10,12] are not suitable mechanisms for the $\delta \rightarrow \gamma$ transition.

Third, one can observe from Fig. 3 that for each one of TiH (*abgh*), $TiH_{1.25}$(*abceg*), and $TiH_{1.5}$ (C_3), the electronic band structure