Energetics and structure of single Ti defects and their influence on the decomposition of NaAlH₄

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The energetics and structure of various types of single extrinsic Ti defects in NaAlH₄ bulk and (001) slab at the hydriding/dehydriding critical point environment were studied systematically. It is found that the most favorable situation is Ti substituting Al at the subsurface (TiAl(2nd)), which has the highest coordination number for extrinsic Ti ions. The most stable Ti defect in the 1st layer is located at the Al rich interstitial site, namely Tii(1st), accompanied with remarkable strength of Ti–H/Al bond and local geometry deformation at the 1st layer around Ti. Deeper insight of the formation mechanism of Ti defects is obtained by dividing the formation enthalpy of Ti defects into three terms, which are contributed from the cost of removing a substituted host atom if necessary, the cost of structure deformation, and the gain of bonding between Ti and its surrounding ions in the formation of the defects. This associates the formation energy directly with the local structure of Ti defects. For the first time, we adopt f(Na), f(H), f(H–H), f(AlH₃) and f(Na) to discuss the hydrogen release ability of the Ti doped NaAlH₄. We find that TiAlH₄, AlH₃ and TiAlH₁₂ complexes are formed around TiAl(2nd) and Tii(1st) respectively, which significantly promotes the dehydriding ability of NaAlH₄. What is more, the catalyst mechanism of Ti on the decomposition of NaAlH₄ is linked to the AlH₃ mechanism according to our calculations.

1. Introduction

Since the discovery that hydriding/dehydriding reversibility and the reaction kinetics of NaAlH₄ can be greatly improved by doping with Ti-containing catalysts, a alanates, amides and borohydrides have become a focus in hydrogen storage materials researches. b,c,d,e,f,g,h,i,j,k,l,m,n,o,p,q,r,s,t,u,v,w,x,y,z Although the importance of Ti-containing catalysts is well recognized, the catalytic mechanism is not well understood.

It is challenging to determine the location and local structure as well as the influence of extrinsic Ti defects in experiments at the atomic level, especially for the materials involving hydrogen atoms. Meanwhile, computational methods are advantageous for these studies of well-defined model systems. Ke et al. e have done an outstanding work on the decomposition reactions of NaAlH₄, Na₃AlH₆ and NaH with first-principles method, and they strongly suggested further investigation on the doped NaAlH₄ system.

Many first-principles studies have been attributed to the catalytic mechanism of Ti defects. Iniguez et al. 5,7 have reported that Ti prefers to substitute Na in the bulk or surface of NaAlH₄ and it would shorten the distance of H–H and facilitate the formation and release of H₂. There are also some reports 8–10 that Ti is favorable to substitute Al in bulk of NaAlH₄, and the corresponding improvement in hydriding/dehydriding behavior is attributed to the formation of Ti–Al bonds, which weaken Al–H bonds nearby. Liu et al. 11–13 showed that Ti is favorable at interstitial sites at the surface and forms TiAlH₁₂ complexes, which may be a precursor of TiAl₃. They suggested that the hydrogen desorption energy is thus considerably smaller than that from a clean NaAlH₄ surface. In addition, Marashdeh et al. 14 showed that Ti is more stable at the subsurface of the NaAlH₄ than on the surface, and prefers to substitute Na ions. They also suggested a zipper mechanism for hydriding of NaAlH₄. Vegge 15 reported that TiNa–2VNa on the surface of NaAlH₄ can lower the barriers for H₂ desorption about 1 eV. Gunaydin et al. 16 suggested that the Ti dopant can assist breaking the H–AlH₃ bonds and that AlH₃ vacancies play an important role in the decomposition of NaAlH₄, though they did not give the detailed location of the extrinsic Ti defects.

Generally, Ti defects with higher formation enthalpy have higher activity, so they also have more remarkable effect on the hydriding/dehydriding performance when present. That is why various kinds of Ti defects can improve the hydriding/dehydriding performance of NaAlH₄ as reported in the above literature results. However, it is obvious that the extrinsic Ti defects with high formation enthalpy have low possibility to form. Therefore, it is necessary to study the detailed energetics and structure of extrinsic Ti defects in order to get an insight of its catalytic mechanism. 5

In this paper, a first-principles method is adopted to study the extrinsic Ti defects in NaAlH₄ systematically. First, we compare as many as possible types of Ti defects (cf. section 3.1). Second, we consider the chemical environment for the formation of Ti defects. The defects introduced in the samples are uniquely
determined by the practical hydriding/dehydriding chemical environment, which can be described by the chemical potentials of components. Therefore, the Ti defects are studied at the chemical environment corresponding to the hydriding/dehydriding critical point \(^{17}\) (cf. section 3.1). Third, the most stable charge state of the extrinsic Ti defects is investigated according to charge neutrality of the Ti doped NaAlH\(_4\) system including as many as possible intrinsic and extrinsic defects. At the balanced Fermi level, we find that the neutral state reflects the most stable charge state of the most crucial extrinsic Ti defects, such as Ti\(_{11}\)(2nd), in the Ti-doped NaAlH\(_4\) at the critical hydriding/dehydriding point. Furthermore, we divide the formation enthalpies of Ti defects into several components based on a virtual process of the defect formation. All of these components have physical meaning and are corresponding to the local structure of the Ti defects. In this way, more details of formation mechanism of the most stable Ti defects can be understood.

Based on the determined favorable location of Ti defects, we further study the energetics of Ti defects with respect to its local structures, which is helpful to understand the influence of Ti on the initial stage of the decomposition of NaAlH\(_4\) with assistance from Ti defects.

### 2. Computational methods

We performed DFT plane-wave calculations of a Ti-doped NaAlH\(_4\) \(2 \times 2 \times 2\) supercell (16 NaAlH\(_4\) units) and a \(2 \times 2\) (001) slab (7 layers of Na/Al cations, 28 NaAlH\(_4\) units) using the VASP code.\(^{18,19}\) The (001) surface is a close packed surface with the lowest surface energy.\(^{19}\) A vacuum space of 15 Å along the \(z\) directions is employed to simulate the surface. The Al and Na ions in the two bottom layers of the slab were fixed during relaxation, while all the H ions are relaxed in order to diminish the influence of surface polarization.\(^{12}\) The Projector Augmented Wave (PAW) potential was used to describe electron–ion interactions and the PW91 GGA approximation\(^{20}\) was employed to calculate exchange and correlation energy. The Brillouin zone was generated by the Monkhorst–Pack scheme with \(5 \times 5 \times 3\) for the supercell and \(5 \times 5 \times 1\) for the slab. The cut-off energy for plane waves was 500 eV.

### 3. Results and discussion

#### 3.1 The formation enthalpies of extrinsic Ti defects

The formation enthalpies of defect were calculated from eqn (1):\(^{21}\)

\[
H_f^{\text{(def)}} = E^{\text{(def)}} - E^{\text{(bulk/slab)}} - \sum_i n_i (\Delta \mu_i + \mu_i^{\text{37S}}) \tag{1}
\]

Here, \(H_f^{\text{(def)}}\) is the defect formation enthalpy; \(E^{\text{(def)}}\) is the calculated total energy of the supercell/slab with defect; \(E^{\text{(bulk/slab)}}\) is the calculated total energy of the supercell/slab without defect. \(\mu_i^{\text{37S}}\) is the chemical potential of component \(i\) in the most stable elemental crystal which is adopted as the reference for convenience. \(\Delta \mu_i\) is the relative chemical potential of component \(i\), and \(\mu_i = \Delta \mu_i + \mu_i^{\text{37S}}\) is the chemical potential of component \(i\) in the real chemical environment. \(n_i\) denotes the number of ions of species \(i\), which is added \((n_i > 0)\) or removed \((n_i < 0)\) during the formation of a defect. It is obvious that the lower \(H_f^{\text{(def)}}\) is, the more stable the extrinsic Ti defect is.

The defect formation enthalpy is influenced by the chemical environment. Therefore, only when the chemical environment corresponding to the practical experimental condition is adopted, the calculated defect formation enthalpies reflect the actual defect stability. Here, the chemical environment is discussed according to the equilibrium of the Ti–Na–Al–H phase diagram (Fig. 1).

Before adding Ti dopants, lines OP, OQ and PQ correspond to the pure Na, H\(_2\) and Al phase, respectively. Lines BC, EF correspond to the critical equilibrium line of NaAlH\(_4\)/Na\(_3\)AlH\(_6\) and NaAlH\(_4\)/AlH\(_3\), respectively. The trapezoid region BCEF corresponds to the stable chemical potential range (SCPR) of NaAlH\(_4\). Points F, C and B correspond to the Na poorest, H\(_2\) poorest, and Al poorest chemical environment, respectively. Hydriding/dehydriding reaction of NaAlH\(_4\) will take place when the chemical potential of H in the environment is higher/lower than that at point C. Therefore, point C is called the hydriding/dehydriding critical point of NaAlH\(_4\). Similarly, point D is the hydriding/dehydriding critical point of Na\(_3\)AlH\(_6\).

As shown in ref. 17, TiAl\(_3\) (blue region) and TiH\(_2\) (green region) competing phases will form in Al rich and H rich areas when \(\Delta \mu_{\text{Ti}} > -1.55\) eV, which leads to a shrinking of the SCPR of NaAlH\(_4\) (black region when doped) and a shift of the hydriding/dehydriding critical point \(\text{(e.g. from C to CTi in Fig. 1)}\). When \(\Delta \mu_{\text{Ti}} > -1.26\) eV, the SCPR of NaAlH\(_4\) disappears, and thus the system can no longer undergo rehydriding. While \(\Delta \mu_{\text{Ti}} < -1.59\) eV, the Ti-containing competing phases do not form and the concentration of Ti defects is too low to catalyse the hydriding/dehydriding in NaAlH\(_4\). In practice, \(\Delta \mu_{\text{Ti}}\) should be tuned to slightly greater than \(-1.59\) eV, which is the maximum value of \(\Delta \mu_{\text{Ti}}\) not affecting the SCPR of pure NaAlH\(_4\). In this paper, we adopt the critical value of \(\Delta \mu_{\text{Ti}} = -1.59\) eV for the analysis of the stability of Ti defects. When \(\Delta \mu_{\text{Ti}} = -1.59\) eV, \(\Delta \mu_{\text{Na}}\), \(\Delta \mu_{\text{Al}}\) and \(\Delta \mu_{\text{H}}\) are corresponding to the values at the critical point of

\[\text{Fig. 1} \text{ The chemical potential phase diagram of Ti–NaAlH}_4\text{. Region BCEF and the black shadowed region corresponds to SCPR of NaAlH}_4\text{ and the points C and CTi are the hydriding/dehydriding critical points of NaAlH}_4\text{ before and after doped with Ti respectively.}\]
NaAlH₄ (point C) since it is not shifted by Ti dopants. Obviously, at this chemical environment, the upper limit of the formation enthalpies of substitutional Ti defects at Al and Na sites are obtained, since $\Delta \mu_{Al}$ and $\Delta \mu_{Na}$ decrease as the hydriding/dehydriding critical point shifts upwards.

In this work, we have considered as many extrinsic Ti defects as possible. From the space aspect, we consider Ti defects located at the 1st layer, the 2nd layer, the 3rd layer as well as in the bulk of NaAlH₄. From the aspect of Ti defect types, we consider interstitial defects at octahedron sites, Ti substituting Na, and Ti exchanging with Na/Al when Ti locates on the surface. The Na–Al bridge site at the 1st layer and tetrahedron interstitial site are not considered because the distance between Ti and its nearest neighbor (NN) ions is too short. We have also calculated other complex defects like TiNa and Ti i. As shown in Fig. 4b, the stability of these Ti defects are difficult to form and we do not discuss them in this paper. All these locations of Ti before structure relaxation are shown in Fig. 2.

It should be pointed out that the situation of Ti located at an octahedron interstitial site is more complicated than the others. There is only one type of octahedron in the bulk of NaAlH₄ which has three Na cations and three Al cations at its vertexes, while there are quite a few interstitial sites near the surface because the translational symmetry disappears along the direction perpendicular to the surface. At the 1st layer, the interstitial sites with 3 NN Al and 2 NN Na cations are referred to “Al-rich” interstitial sites, while “Na-rich” interstitial sites are surrounded with 2 NN Al and 3 NN Na cations (cf. Fig. 2). They are denoted by $\text{T}_{i}\text{Al}(1st \text{ Al rich})$ and $\text{T}_{i}\text{Al}(1st \text{ Na rich})$, and the former is simplified to $\text{T}_{i}\text{Al}(1st)$ due to its lower formation enthalpy in the text later. Besides, we have considered Ti defects locating at the 2nd layer octahedron interstitial site with Na/Al at the top of it (cf. Fig. 3l and 3I).

The local structures of Ti defects after structure relaxation are shown in Fig. 3. It shows that the neighbor H and Al ions are attracted by Ti while Na cations nearby are repulsed, because Ti has good affinity with Al and H but not with Na. As a result, Ti–H₈ or Ti–Alₓ–Hₙ complex forms around Ti. There is an obvious difference between any two relaxed Ti-containing local structures of different types, while Ti-containing local structures with the same type are similar to each other except the situation of Ti at the 1st layer. Generally, the relaxed local structures of Ti-containing complexes are not similar unless the distribution of Na/Al/H ions around Ti before relaxation is similar. We highlight some ions near Ti for a better visualization. For interstitial Ti defects, we highlight the TiAl₁H₁₂ complex in accordance with an earlier reported structure.$^{11-13}$ For Ti substituting Na situations, the TiH₈ (TiH₈ at 1st layer) complexes were highlighted in line with the work by Løvvik et al.$^{8}$ As for Ti substituting Al situations, we highlight the TiAl₄H₂₀ (TiAl₄H₂₀ at 1st layer) complex in Fig. 3.

$H(\text{def})$ of the Ti defects at different depths in the (001) slab of NaAlH₄ are shown in Fig. 4a. It is obvious that the defect of Ti substituting Al at 2nd layer, labeled with TiAl₂(2nd) (Fig. 3k), is the most stable among all the Ti defects which is consistent with Løvvik et al.$^{8}$ Its formation enthalpy at the hydriding/dehydriding critical point is 2.01 eV. In the 1st layer, Ti is most favorable at the Al rich interstitial site, $\text{T}i\text{i}(1st)$ (Fig. 3e), which is in accordance with the result in ref. 12, and its formation enthalpy $H(\text{def})$ is 3.08 eV at the hydriding/dehydriding critical point. In addition, from the space aspect, $H(\text{def})$ is obviously higher than others when Ti locates outside of 1st layer metal of (001) slab. From the aspect of defect type, $H(\text{def})$ of Ti exchanging with surface Na/Al and Ti on the surface are so high that they are difficult to form. Therefore, in the following, we only consider three types of extrinsic Ti defects: TiAl₁, TiNa, and Ti i.

Fig. 4b is plotted for a convenient comparison of the formation enthalpies of the three types of Ti defects: TiAl₁, TiNa, and Ti i. As shown in Fig. 4b, the stability of these Ti defects at the same layer in the sequence from high to low is TiAl₁ > TiNa > Ti i except the Ti i(1st). For defects of Ti substituting Na, the stability of Ti defect reduces gradually with increase of its depth in slab. For Ti i defects at the 1st layer, the formation enthalpy in Al rich interstitial sites is much lower than that in Na rich interstitial sites, while the difference between different interstitial sites at the 2nd layer is much smaller. If only the Ti i defects with lower formation enthalpy at a layer is considered, the stability of defect reduces gradually with its depth increasing. As for the defect of Ti substituting Al type, TiAl₂(2nd) is the most stable one. There are little difference for $H(\text{TiAl})$ in different layers except TiAl₂(2nd). For all types of Ti defects, the defect formation enthalpy in the 3rd layer has no remarkable difference with that in bulk.

From above results, TiAl₂(2nd) is obviously the most stable extrinsic Ti defect in NaAlH₄. However, considering that there are kinetic barriers before Ti reaches TiAl₂(2nd) site when it migrates from outside of NaAlH₄, we expect that most Ti defects may initially be formed at the 1st layer. $H(\text{TiAl₁})$ is the lowest among Ti defects near the 1st layer at the hydriding/dehydriding critical point, and it was studied by Liu et al.$^{11-13}$ Furthermore, the Ti site of Ti i(1st) is right on the top of that of
Ti\textsubscript{Al}(2nd), and the former defect may be a precursor of the later one. Therefore, Ti\textsubscript{i}(1st) also plays a crucial role in the Ti catalysis for dehydrogenation. We will discuss the influence of TiAl\textsubscript{2}(2nd) and Ti\textsubscript{i}(1st) on decomposition of NaAlH\textsubscript{4} in a later section.

### 3.2 Decomposition of $H_f^{\text{def}}$

Here, we decompose $H_f^{\text{def}}$ in accordance with a virtual process of the defect formation. We presume that the formation process of a Ti defect can be divided into three stages, exemplified with the Ti\textsubscript{Na} defect in the following.

Firstly, it costs energy of $H_f(V_{Na})$ to remove one Na atom from the bulk of NaAlH\textsubscript{4} i.e., the formation of $V_{Na}$. Next, a Ti atom from the environment is put into the vacancy site and has its neighbor ions adjusting their position without considering the bonding between Ti and its surrounding (energetic-wise). It will cost a deformation energy, $E_d(TiM)$. Finally, Ti atom will bond with its surrounding ions with an energy gain of $E_b(TiM)$. Thus, the formation enthalpy of a Ti defect can be expressed as the sum of three terms:

$$H_f(TiM) = E_d(TiM) + H_f(V_M) - E_b(TiM) \quad (M = Al, Na, i)$$

Here, “i” means “octahedral interstitial site”, and obviously that $H_f(V_i) = 0$. It should be pointed out that $E_d(TiM)$, $E_b(TiM)$ and $H_f(V_M)$ have physical meanings and can be calculated by a first-principles method. Furthermore, they are closely related to the local structure of defect site which is of advantage in discussing the formation mechanism of Ti defects by combining those energies with Ti-containing local structure.

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**Fig. 3** Relaxed local structures of Ti-containing complexes in Ti-doping model and AlH\textsubscript{4} complex in clean (001) slab. (a)-(o) correspond to the Ti defect at surface, subsurface and the third layer, which are arranged by the Z coordination of Ti from large to small in the NaAlH\textsubscript{4} (001) slab. (a): Ti at Al site on surface; (b): Ti at surface Na rich interstitial site [Ti\textsubscript{i}(1st Na rich)]; (c): Ti at Na site on surface; (d): Ti exchanging with surface Na [Ti\textsubscript{Na–NaAl}(1st)]; (e): Ti at surface Al rich interstitial site [Ti\textsubscript{i}(1st Al rich)]; (f): Ti substituting surface Al [Ti\textsubscript{Al}(1st)]; (g): Ti substituting surface Na [Ti\textsubscript{Na}(1st)]; (h): Ti exchanging with surface Al [Ti\textsubscript{1Al–Al\textsubscript{i}(1st)}]; (i): Ti at 2nd layer interstitial site with Al at top [Ti\textsubscript{i}(2nd,Al\textsubscript{top})]; (j): Ti substituting the 2nd layer Na [Ti\textsubscript{Na}(2nd)]; (k): Ti substituting the 2nd layer Al [Ti\textsubscript{Al}(2nd)]; (l): Ti at 2nd layer interstitial site with Na at top [Ti\textsubscript{i}(2nd)]; (m): Ti at 3rd layer interstitial site [Ti\textsubscript{i}(3rd)]; (n): Ti substituting the 3rd layer Al [Ti\textsubscript{Al}(3rd)]; (o): Ti substituting the 3rd layer Na [Ti\textsubscript{Na}(3rd)]; (p): Ti substituting Al in bulk [Ti\textsubscript{Al}(bulk)]; (q): Ti substituting Na in bulk [Ti\textsubscript{Na}(bulk)]; (r): Ti at interstitial site of bulk [Ti\textsubscript{i}(bulk)]; (s) clean (001) slab.
$H_f(TiM)$ is increased by $E_d(TiM)$ and reduced by $E_b(TiM)$, while the bonding and deformation energy induced by Ti are correlative. We know that the displacement of neighbor Al/H/Na occurs during relaxation when Ti ion bonds with its neighbor Al/H ions, which should be balanced in the end. It is easy to know that a stronger attraction between Ti and its neighbor Al/H ions needs to be balanced by a greater deformation around the Ti ion in principle. We can see later in Fig. 6 that if the configuration of Ti-containing complexes are similar, higher $E_b(TiM)$ corresponds to higher $E_d(TiM)$ and lower $H_f(Ti_{def})$. Therefore, the stability of Ti defects can be described qualitatively by either the bonding or deformation degree, which is originated from the attraction between Ti and its neighbor ions. In this paper, we describe the stability with structural parameters of Ti defects of the same type.

The structural parameters of TiAl type of defects are shown in Fig. 5a. It is clear that the related distances of Ti–NN H in the four situations (Fig. 5a) are almost the same, and much shorter than $d(TiH_2)$, the Ti–H bond length in TiH$_2$ (about 1.90 Å). This is due to the formation of similar compact TiH$_4$ complexes in all the Ti substituting Al situations. Accordingly, the contribution of the TiH$_4$ complex to the deformation and bonding energy is almost the same in these four situations. Hence, the structures outside of the TiH$_4$ complexes become decisive for the relative stability of the Ti substituting Al defects. Regarding the local structure, Ti$_{Al}$(1st), which has no NN AlH$_4$ complexes above Ti (Fig. 3l), is obviously different from the other three situations (cf. Fig. 3k, n and p). All the structural parameters show little difference between bulk Ti$_{Al}$(bulk) and Ti$_{Al}$(3rd) situation (cf. open circles and open squares in Fig. 5a). The corresponding Ti–X (X = H, Al) distances in the Ti$_{Al}$(2nd) situation are clearly shorter than those in Ti$_{Al}$(bulk) and Ti$_{Al}$(3rd) situations. Especially, the two Ti–Al distances above Ti is very close to $d(TiAl_3)$, the Ti–Al distance in bulk TiAl$_3$ (about 2.72 Å), indicating that Ti has a greater coordination number (CN) in the Ti$_{Al}$(2nd) situation. The distance of two Ti–Al above Ti is shorter than that of the two under Ti, because the constraint in surface is looser. Obviously, the stability of Ti$_{Al}$(2nd) is higher than Ti$_{Al}$(bulk) and Ti$_{Al}$(3rd) from the structural analysis. As for the Ti$_{Al}$(1st) situation, although all the corresponding Ti-related bond lengths are very close to those in Ti$_{Al}$(2nd) situation, the CN of Ti is less due to the surface boundary. In summary, Ti$_{Al}$(2nd) is obviously the most stable one among the four Ti$_{Al}$ dopants from the structural analysis. Similarly, from the structural analysis, the bonding energy in the Ti$_{Na}$(1st) situation are more stable than that in the Ti$_{Na}$(bulk), Ti$_{Na}$(3rd) and Ti$_{Na}$(2nd) situation.

The structural parameters of the interstitial type of Ti defects are shown in Fig. 5c, where the situation for the 3rd layer is excluded since there is no remarkable difference found between the 3rd layer and bulk Ti defects in the previous studies. For Ti–X (X = H, Al) distances of Ti-containing complexes, it is similar to the Ti$_{Al}$ and Ti$_{Na}$ situations that there is little difference between Ti$_i$(bulk) and Ti$_i$(2nd). Furthermore, it is shown in Fig. 5c that the distances of Ti–(NN Al) under Ti in the Ti$_i$(1st) situation is obviously shorter than that in other two situations. As for other Ti–X (X = H, Al) distances of Ti-containing complexes, their contribution is almost equal to the Ti-binding energy. Consequently, from the structural analysis, Ti$_i$(1st) is slightly more stable than the other two defects.

$E_d(TiM)$, $E_b(TiM)$, $H_f(V_M)$ (M = Al, Na, i), as well as $H_f(TiM)$ of the three types of extrinsic Ti defects in bulk and...
The near surface region of NaAlH₄ are shown in Fig. 6. For Ti₁₃ defects in Fig. 6a, \( E_b(TiM) \) of Ti₁₃(2nd) is the highest, which is consistent with the shorter Ti-related bonds and higher CN of Ti in the structure (Fig. 5a). When Ti is located at surface, the binding energy of Ti is the lowest, which is mainly due to its low CN. The value of \( H_f(V_M) \) decreases as the depth of Ti decreases. We know that AlH₄ is a rather stable complex which makes the formation of Al vacancies difficult. The local structures of Al vacancies are shown in Fig. 7 and we can see there are a lot of changes. The high energy “4H local structure” in Ti₁₃(bulk) situation (Fig. 7a) leads a high vacancy formation enthalpy, while the Al vacancy formation enthalpies near the surface are much lower because of their more stable 2(H–H) local structure (Fig. 7b). The deformation energy in the bulk situation is lower than that near the surface and it is also consistent with analysis of the local structures. The \( E_d(TiM) \) is rather high which is due to large displacement of the NN H/Al ions relative to the Al vacancy local structure. In Ti₁₃(2nd), Ti₁₃(3rd) and Ti₁₃(bulk) situations the Ti-containing complexes are similar, and it is shown in Fig. 6a that among these three situations, a higher binding energy corresponds to a higher deformation energy and lower \( H_f(Ti\text{ def}) \).

In the Ti₁₃ case (Fig. 6b) the difference between the values of \( H_f(V_M) \) among the three different defects is not remarkable. We can see that the values of \( E_b(TiNa) \) and \( E_d(TiNa) \) increase while \( H_f(V_M) \) decreases with decreasing depth of Ti defects, which is due to a looser constraint on the surface. The changes in \( E_b(TiNa) \) and \( E_d(TiNa) \) are also consistent with the corresponding structure relaxation. As a result, Ti is favorable at the 1st layer among all the Na vacancies. Just like in Ti₁₃, TiNa(2nd), TiNa(3rd) and TiNa(bulk) situations, a higher binding energy corresponds to a higher deformation energy and a lower \( H_f(Ti\text{ def}) \).

The energy information for the interstitial type of Ti defects is shown in Fig. 6c. There is little difference in each energy term for the different locations of Ti; viz. the 2nd layer vs. bulk. The binding energy in Ti₁₃(1st) situation is the greatest while the deformation energy in this situation is the lowest, which seems contradictory at first sight. However, we find in the deformation aspect that the NN Na–Na distance (a parameter for Na–Al octahedron deformation) above Ti in the Ti₁₃(1st) situation is much longer than the other two situations. Besides, the displacement of Al under Ti is 0.295/0.63/0.63 Å for Ti located at the 1st layer/the 2nd layer/bulk, respectively. This implies that the structural
deformation of Tii(1st) is greater than others, but it occurs mainly at the 1st layer where has less constraints. It is understandable that Tii(1st) is the most favorable interstitial Ti defect.

From our calculation, the extrinsic Ti defects are favorable to locate at the 1st and 2nd layer, while they are difficult to enter deeper layers. This is consistent with the AES experiment by Gross et al., and the EXAFS and XANES experiments by Balde et al. It is easy to imagine that Ti accumulates at the shallow surface as its doping amount increases, probably followed by the formation of a Ti-rich interface between NaAlH4 and the Ti-containing substance. We know that the local structure of Ti defects is of a Ti–Al–H complex, which means that there is a competition between the H–Ti phases and Al–Ti phases when the amount of Ti increases. Although the formation ability of TiAl3 phase is the highest under the global thermodynamic equilibrium state under the H-poor hydriding/dehydriding critical point environment, it is difficult to form TiAl3 crystals due to the competition between H–Ti and Al–Ti phases. This could be the reason that amorphous Ti-containing substance is often be found in experiments.

The Ti-rich layer should be characterized further, because this tight coupling interface probably plays a key role in catalysis of the gas–solid reaction of the Ti–NaAlH4 system.

3.3 Local geometry structure of Tii(2nd) and Tii(1st) defects

We now compare the local structures around Ti for Tii(2nd) and Tii(1st) cases in detail (Fig. 8 and 9) which is helpful to reveal the geometry structure change. Since the influence of Ti on NaAlH4 is neighboring regions of both Ti–Al–H complexes have obvious situations, respectively. In addition to the Ti–Al–H complexes, (a) side view; (b) top view.

![Fig. 8 Relaxed local structures around Ti in the Tii(1st) situation: (a) side view; (b) top view.](image-url)

![Fig. 9 Relaxed local structures around Ti in the Tii(2nd) situation: (a) side view; (b) top view.](image-url)

Tii(1st) situation are larger than that in Tii(2nd) situation, especially the Na1 and Na2 ions. Besides, a greater displacement of Na corresponds to a greater displacement of Al. This also shows that the 2nd NN AlH4 groups of Ti (cf. Al4–H13–16 in Fig. 8 and Al5–H21–24 in Fig. 9) are also influenced greatly by the Ti defects in both situations, especially for the Tii(1st) situation. The deformation of AlH4 groups in the “surrounding region” is mainly AlH3–H separation in both situations. Corresponding to a greater displacement of Al, the AlH3–H separation in Tii(1st) situation is more significant. The reason for AlH3–H separation is related to the fact that the AlH3 is a magic cluster of Al4 due to its high stability.

The configuration of each Ti-containing complex is more complicated than the related “surrounding region” in both situations. In the Tii(1st) situation, the distance between Ti and the three NN AlH4 groups is very short before relaxation, and the three NN AlH4 groups are influenced greatly by Ti. After relaxation (Fig. 8), the distances between Ti and the three Al are remarkably shorter than d(TiAl3), which means that those Ti–Al bonds are very strong. Furthermore, all the three NN AlH4 groups are destroyed, thus, the deformation of them are not just AlH3–H separation. The NN H ions of Ti in the three NN AlH4 groups are captured by Ti, i.e., these H ions are bonded with Ti mainly (H1,10 in Fig. 8). The 2NN H ions in the three NN AlH4 groups move close to Ti greatly, and they bond with both Al and Ti, denoted as “bridge H”. (H1,6 in Fig. 8). The remaining H ions are bonded with Al mainly (H1,4 and H11,12 in Fig. 8). Consequently, H ions in Ti-containing complexes can be divided into three types based on bonding condition: Ti, H ions bonded with Al mainly; T3, bridge H; T3, H ions bonded with Ti mainly. In addition, the deformation in the Tii(1st) situation is at the 1st layer mainly.

In the Tii(2nd) situation, the distance between Ti and its four NN H ions are very short, as mentioned above, due to a compact TiH4 form (H9–12 in Fig. 9). The distances of Ti–(NN H) in TiH4 are shorter than the shortest distance of Ti–(NN H) in the TiAl3H12 complex. According to the 18e rule, the TiH4 structure is unstable and Ti needs to attract the four NN AlH4 groups for a further relaxation. Among the four NN AlH4 groups, those H ions with shortest distance to Ti move towards the Ti and become “bridge H” (H7,8 and H13,14 in Fig. 9). Similar to the Tii(1st) situation, the deformation of the NN AlH4 groups of Ti in the Tii(2nd) situation are not limited to AlH3–H separation, while the deformation degree in

3.4 Influence of the two stable Ti defects on the decomposition of NaAlH4

The hydrogen release ability is often characterized by \( H(V_{Na}) \). Later, Liu et al. adopted \( H(V_{Al-H}) \) as another criterion. Furthermore, Fu et al. reported that \( (AlH_3)_n \) is released during the hydriding/dehydriding of NaAlH4. Gunaydin et al. also pointed out that the AlH vacancy plays an important role on the decomposition of NaAlH4. In addition, Araujo reported that Na vacancy can promote the decomposition of NaAlH4. Here, we adopt all of \( H(V_{Ti}), H(V_{Ti-Al-H}), H(V_{AlH}), \) and \( H(V_{Na}) \) as the score card of the influence of the extrinsic Ti defects on NaAlH4 decomposition. The formation enthalpies of these four vacancies are symbolized as \( H(V_{vacancy}) \) later. Generally, there are quite a few configurations for each type of vacancy due to the complicated local structure around Ti. The configuration with minimum formation enthalpy at the hydriding/dehydriding critical point is a natural choice for each type of vacancies and they are listed in Table 1 and Table 2 and illustrated in Fig. 10.

We can see that the formation energies of all the four vacancies are lower when Ti is introduced, which means that the Ti dopants play a critical role on promoting the decomposition of NaAlH4. Since the configurations within Ti-Al–H complexes are more complicated than the “surrounding region”, here we discuss the vacancies in “surrounding region” firstly.

From Tables 1 and 2 and Fig. 10, we conclude that:

(i) All the \( H(V_{Na}) \) decrease significantly when extrinsic Ti defects are introduced, especially in the Ti1(1st) situation. An important reason for the reduction of \( H(V_{Na}) \) around Ti defects is that Na ions are pushed away significantly by the Ti defect in the “surrounding region” of TiAlH2 and TiAlH12 complexes, which can be seen from the geometric structure, and the displacement of Na in the latter situation is noticeably greater. The activity of Na increases when Na atom deviates from the original equilibrium site, which makes \( H(V_{Na}) \) decrease. Therefore, \( H(V_{Na}) \) in Ti1(1st) situation is smaller than that in the TiAl(2nd) situation because of the greater displacement of Na in the former situation.

(ii) Both \( H(V_{AlH}) \) and \( H(V_{H}) \) decrease in the “surrounding region” of the two Ti–Al–H complexes, especially in the Ti1(1st) situation. From the structure aspect, the AlH4 complex in the clean (001) slab transforms to an AlH3–H structure when Ti is introduced. As a result, the AlH4 complex is easy to break into two units: H and AlH3. Therefore both \( H(V_{AlH}) \) and \( H(V_{H}) \) corresponding to the AlH3–H configuration are lower than that in AlH4 of the clean slab. The displacement of Al4 in Ti1(1st) case is greater than that of Al4 in the TiAl(2nd) case. Accordingly, the separation of AlH3–H in the Ti1(1st) case is more marked. It is the main reason that both \( H(V_{AlH}) \) and \( H(V_{H}) \) in Ti1(1st) case are lower than that in the TiAl(2nd) situation. This is consistent with Gunaydin’s proposal that Ti plays a role in the catalytic breaking of AlH3–H bonds.

Now we compare vacancies within the two Ti–Al–H complexes with a focus on \( H(V_{Ti}) \). At first, \( H(V_{Ti}) \) of type T1 H ions in the TiAlH3 complex is lower than that in the TiAlH12 complex, because the corresponding Al–H bond length in TiAlH3 complex is longer (1.676 Å vs. 1.669 Å). Similarly, the \( H(V_{Ti}) \) for H of type T1 in the TiAlH3 complex is lower than that in the TiAlH12 complex, which is reflected by the relation of their Ti–H bond lengths (1.860 Å vs. 1.852 Å). The \( H(V_{Ti}) \) for H of type T1 is lower than that of type T1 in both Ti-containing complexes, because the affinity of Ti–H is stronger than that of Al–H. Furthermore, it is shown that the bridge H (T2) has a greater \( H(V_{Ti}) \) than H of types T1 and T3 in both Ti-containing complexes, and \( H(V_{Ti}) \) of T2 type H in the TiAlH12 complex is higher than that in the TiAlH30 complex. Regarding the structural parameters, the Al–H–Ti–H distance corresponding to T2 type of H is 1.78/1.819 Å and 1.78/1.926 Å in TiAlH30 and TiAlH12, respectively, which means that the latter has a longer bond length but a greater \( H(V_{Ti}) \). In addition, it is shown that the \( H(V_{Ti}) \) for the three types of H in both situations with the Ti defects are lower than that in the clean (001) slab, which is consistent with

<table>
<thead>
<tr>
<th>Vacancy</th>
<th>( H(T_i) )</th>
<th>( H(T_2) )</th>
<th>( H(T_3) )</th>
<th>H–H</th>
<th>AlH3</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration of defect (in complex)</td>
<td>( H_1 ), ( H_2 )</td>
<td>( H_2 ), ( H_3 )</td>
<td>( H_4 ), ( H_5 )</td>
<td>( H_1 ) &amp; ( H_4 )</td>
<td>( Al_1 ) &amp; ( H_2 ) &amp; ( H_4 ) &amp; ( H_6 )</td>
<td>0.34</td>
</tr>
<tr>
<td>Configuration of defect (surrounding region)</td>
<td>( H_{21} )</td>
<td>( H_{21} ), ( H_{33} )</td>
<td>( H_{23} )</td>
<td>( H_{21} ) &amp; ( H_{33} )</td>
<td>( Al_1 ) &amp; ( H_2 ) &amp; ( H_3 ) &amp; ( H_23 ) &amp; ( H_{24} )</td>
<td>( Na )</td>
</tr>
<tr>
<td>In clean (001) slab</td>
<td>( H_1 )</td>
<td>( H_1 ) &amp; ( H_2 )</td>
<td>( H_1 ) &amp; ( H_2 )</td>
<td>( Al_1 ) &amp; ( H_1 ) &amp; ( H_2 ) &amp; ( H_3 )</td>
<td>( Na )</td>
<td>3.63</td>
</tr>
</tbody>
</table>

\( ^a \) Symbol “,” means “logic or”, \( ^b \) Symbol “&” means “logic and”. View Online
conclusions from earlier reports\textsuperscript{9,11} that the formation of Ti–Al can weaken Al–H bonds. The results are not straightforward. We can see that a stronger Ti–Al bond in TiAl\textsubscript{3}H\textsubscript{12} complex does not correspond to a lower \( H_f(\text{V}_{\text{H}_1/2}) \), but actually higher than that in TiAl\textsubscript{4}H\textsubscript{20} complex. Liu et al.\textsuperscript{13} considered that the TMAl\textsubscript{3}H\textsubscript{12} (TM = Sc–Co) complexes follow the 18-electron rule\textsuperscript{28} whereas the TiAl\textsubscript{3}H\textsubscript{12} complex is a 2e electron-deficient complex. If the TiAl\textsubscript{3}H\textsubscript{20} complex also obeys the 18-electron rule, it is a one-electron-rich complex which is in line with its low \( H_f(\text{V}_{\text{H}_1/2}) \) of H\textsubscript{1}/H\textsubscript{2} (Fig. 10). Furthermore, it was reported that the electronic population on the Al–H bond is 0.88 and clearly the covalent bond dominates the interaction between H and Al.\textsuperscript{7} There are also hybridization between Al and Ti in TiAl\textsubscript{3}.\textsuperscript{9} Those results indicate that the interaction between Ti and Al is also dominated by the covalent bond. Owing to the saturation property of the covalent bond, it is expected that the bond strength of Ti–H and Ti–Al would decrease when the CN of Ti increases to some extent, consistent with that reported by Vajeeston et al.\textsuperscript{31} We know that the CN of Ti in the electron-rich TiAl\textsubscript{4}H\textsubscript{20} complex are higher than that in the TiAl\textsubscript{3}H\textsubscript{12} complex, which is an important reason for the lower \( H_f(\text{V}_{\text{H}_1/2}) \) in the TiAl\textsubscript{3}H\textsubscript{30} complex.

After the comparison of vacancy formation energies between the two Ti–Al–H complexes, it is necessary to make a comparison between the “surrounding regions” and the complexes themselves. It is easy to see from Fig. 10 that \( H_f(\text{vacancy}) \) values in the TiAl\textsubscript{3}H\textsubscript{12} complex are lower than that in its “surrounding region”, except for \( H_f(\text{V}_{\text{AlH}_3}) \) of the TiAl\textsubscript{3}H\textsubscript{12} complex possibly due to the weakened Al–H bond strength by the formation of Al–Ti bonds. On the other hand, in the “surrounding region” all the related \( H_f(\text{vacancy}) \) are higher than those in TiAl\textsubscript{4}H\textsubscript{30} complex. In addition, there is another reason that the deformation in the “surrounding region” is obviously smaller than that within the complex in TiAl\textsubscript{3}(2nd) situation.

Generally, the H–H and AlH\textsubscript{3} complex vacancies are more complicated than single vacancies, because it involves combination of some single vacancies. We found that the lowest \( H_f(\text{V}_{\text{H}_1/2}) \) correspond to two H of type T\textsubscript{1} with short distance. As for \( H_f(\text{V}_{\text{AlH}_3}) \), it leads to a “crossover” in Fig. 10 (marked by ellipses). According to Tables 1 and 2 and Fig. 10, the value of \( H_f(\text{V}_{\text{AlH}_3}) \) in these situations are expected to follow the order of C < A < D < B. On the other hand, the distance between Ti and its neighbor AlH\textsubscript{4} groups before structure relaxation can be arranged from short to long as C < A < D < B, which is corresponding to the sequence of the strong to weak interactions. \( H_f(\text{V}_{\text{AlH}_3}) \) in those situations (labeled as A, B, C and D) can be sequenced from low to high as D < A < C < B. In the AlH\textsubscript{3}–H separation. Especially, the structure of the 2NN AlH\textsubscript{4} in case C turns to be higher than that in TiAl(2nd) situation.

Generally, the H–H and AlH\textsubscript{3} complex vacancies are more complicated than single vacancies, because it involves combination of some single vacancies. We found that the lowest \( H_f(\text{V}_{\text{H}_1/2}) \) correspond to two H of type T\textsubscript{1} with short distance. As for \( H_f(\text{V}_{\text{AlH}_3}) \), it leads to a “crossover” in Fig. 10 (marked by ellipses). According to Tables 1 and 2 and Fig. 10, the value of \( H_f(\text{V}_{\text{AlH}_3}) \) in these situations are expected to follow the order of C < A < D < B. On the other hand, the distance between Ti and its neighbor AlH\textsubscript{4} groups before structure relaxation can be arranged from short to long as C < A < D < B, which is corresponding to the sequence of the strong to weak interactions. \( H_f(\text{V}_{\text{AlH}_3}) \) in those situations (labeled as A, B, C and D) can be sequenced from low to high as D < A < C < B. In the AlH\textsubscript{3}–H separation. Especially, the structure of the 2NN AlH\textsubscript{4} groups is influenced greatly in case C. It is expected that the complicated bonding hinders the release of AlH\textsubscript{3} in case C. As a result, \( H_f(\text{V}_{\text{AlH}_3}) \) in case C turns to be higher than that in cases D and A. Therefore, an optimal interaction strength between Ti and the AlH\textsubscript{4} group is expected to minimize \( H_f(\text{V}_{\text{AlH}_3}) \), which may be applied to the situation of other transition metal defects in NaAlH\textsubscript{4}.

As shown in Fig. 10, in the Ti\textsubscript{i}(1st) situation, the lowest vacancy formation enthalpy is \( H_f(\text{V}_{\text{AlH}_3}) \), which characterizes the influence of Ti\textsubscript{i}(1st) on the decomposition of NaAlH\textsubscript{4}. In the TiAl(2nd) situation, the lowest vacancy formation enthalpy is \( H_f(\text{V}_{\text{H}_1}) \), but it is not suitable for describing the H\textsubscript{2} release ability in this situation. This is because H\textsubscript{2} is always released after H–H is formed at a small local region of NaAlH\textsubscript{4} matrix, but not assembled by two free H atoms escaping from the NaAlH\textsubscript{4} matrix. Therefore, the hydrogen release ability should be described with \( H_f(\text{V}_{\text{AlH}_3}) \) and \( H_f(\text{V}_{\text{H}_1/2}) \) in TiAl(2nd)
situation. Generally, the low $H_f$($V_{\text{AlH}_3}$) in these two situations are consistent with the AlH3 mechanism of NaAlH4.16,30,32 Therefore, it is a key factor for the dehydriding of NaAlH4 to lower the value of $H_f$($V_{\text{AlH}_3}$). On the other hand, it also implies that increasing the formation ability of AlH3 as well as the interaction energy between the (AlH3)$_m$ molecules and Ti defects will promote rehydriding ability of NaAlH4.33

4. Charged Ti defects in bulk and surface range

Now we consider the stable charge state of the extrinsic Ti defects by calculating the $H_f$ of charged Ti0(bulk), Ti1+ (bulk) and Ti2+ (bulk) as well as Ti3+ (1st), Ti4+ (2nd) and Ti5+ (1st). Five oxidation states of Ti (Ti0, Ti1+, Ti2+, Ti3+ and Ti4+) are taken into account. The charged defect formation enthalpies are calculated by eqn (3):21

$$H_f^{\pm}(E_f, \mu) = E^{\pm} - E^{\text{bulk}} + \sum_i n_i \mu_i + q[E_s^{\text{bulk}}]$$

(3)

Here, $E^{\pm}$ is total energy with/without defect respectively; $E_s^{\text{bulk}}$ is the energy at the valence band maximum (VBM) in bulk/slab without defects. Our calculated value, 4.75 eV, is adopted here for the band gap of NaAlH4, since we cannot find any experimental value. Here the image charge correction34 (typically within 200 m eV) is not employed, which is not expected to affect our conclusion here. The change of the defect formation enthalpies of the above mentioned six Ti defects with respect with the Fermi level is shown in Fig. 11.

The Fermi level of NaAlH4 is pinned by $V_{\text{Na}}$ and $V_{\text{AlH}_4}^+$ in the undoped NaAlH4 according to the overall charge neutrality, which is around 3.30 eV above the VBM of bulk NaAlH4.32 It is shown in Fig. 11 that the Fermi level is still pinned by the intrinsic vacancies of $V_{\text{Na}}$ and $V_{\text{AlH}_4}^+$ when extrinsic Ti defects are introduced. We find that, even in the situation of Ti-richest condition (i.e. $\Delta E_{\text{Ti}} = 0$ eV), Ti dopant has little influence on the equilibrium Fermi level (a global parameter) of NaAlH4, although the total concentration of Ti defects is much lower than those of $V_{\text{Na}}$ and $V_{\text{AlH}_4}^+$, their influence on the surface region could be remarkable since they are accumulated at the surface region.

When the Ti defects are located in the bulk of NaAlH4, Ti0(bulk), Ti1+ (bulk) and Ti2+ (bulk) exist in 0, 0 and +1 charged states, respectively, at the equilibrium Fermi level. The difference between $H_f$($V_{\text{Na}}$) and $H_f$($V_{\text{AlH}_4}^+$) is small, because the transition state of Ti2+ (bulk)/Ti3+ (bulk) are close to the pinned Fermi level. Hence, the order of the defect formation enthalpies is not changed with the consideration of stable charge state, i.e., $H_f$($V_{\text{Na}}$) $<$ $H_f$($V_{\text{AlH}_4}^+$) $<$ $H_f$($V_{\text{AlH}_4}^+$).

5. Conclusion

The extrinsic Ti defects of NaAlH4 have been systematically studied using the DFT method with plane-wave basis set and PAW potentials under the hydriding/dehydriding critical point environment. The following conclusions can be made:

(1) Ti0 (2nd) is the most favorable single Ti defect in NaAlH4, while Ti1+ (1st) is the second favorable one and dominates in the 1st layer of the (001) slab. All the $H_f$ defects in both Ti0 (2nd) and Ti1+ (1st) situations are lower than the corresponding $H_f$ defects in a clean (001) slab of NaAlH4, and thus Ti promotes the decomposition of NaAlH4.

(2) In the “surrounding region” of complexes, all the $H_f$ defects in Ti0 (1st) situations are higher than that in Ti0 (2nd) complex, while within the Ti-containing complex all the $H_f$ defects in Ti1+ (1st) situations are lower than those in the Ti0 (2nd) situations. This is due to a greater deformation in the “surrounding region” as well as a stronger coupling inside the TiAl3H12 complex with respect to the TiAl4H20 complex.

(3) $H_f$($V_{\text{AlH}_4}^+$) can characterize the hydrogen release ability of NaAlH4 in both Ti0 (2nd) and Ti1+ (1st) complexes, and $H_f$($V_{\text{AlH}_4}^+$) in Ti0 (2nd) situation is also a good choice for the scorecard of the hydrogen release ability of NaAlH4.

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