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Role of titanium in hydrogen desorption in crystalline sodium alanate

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The role of Ti in improving the thermodynamics of hydrogen desorption in crystalline sodium alanate (NaAlH_4) has been investigated by using the density functional theory. The total energy calculations reveal that Ti prefers to occupy the Na site over that of the Al site when the atomic energies are used as the reference. However, the use of the cohesive energies of Al, Na, and Ti leads to the Al site being the least unfavorable one. Irrespective of whether Ti occupies the Na or the Al site, the energy necessary to remove a hydrogen atom from Ti substituted sodium alanate is significantly lowered from that of the pure alanate. The understanding gained here may help in designing hydrogen storage materials suitable for industrial applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.1953882]

Interaction of hydrogen in matter has been a topic of interest for more than a century. While the early interest in hydrogen was motivated by the deleterious effects¹ it has on the mechanical stability of materials, the recent interest stems from the hope that hydrogen may be used in clean and renewable energy production processes as well as an energy carrier.² It is generally accepted³ that the biggest hurdle in achieving successful hydrogen-based economy lies in our ability to find a safe, efficient, and cost-effective means for storing hydrogen. In respect to that, a great deal of attention has been paid to the study of complex alkali alanates (MAlH_4 , $\text{M}=\text{Li}, \text{Na}$) (Ref. 4) mainly due to their high hydrogen content. In these compounds, however, the hydrogen atoms are held by strong ionic and covalent bonds resulting in higher dissociation temperatures and slower hydrogen absorption/desorption kinetics than those ones desired for practical applications. Such limitations were demonstrated to be overcome by the addition of Ti-based catalysts.⁵ This important finding has led to a great deal of excitement. However, a full understanding of how and why Ti accomplishes this task is still lacking.

A number of experiments involving x-ray Diffraction, neutron and Raman scattering, and electron spectroscopy have yielded conflicting results. While some of them suggest that Ti occupies the Na sites in the bulk lattice,^{6,7} others report the presence of Ti on the surface in the form of amorphous Ti–Al alloys.^{8–10} A recent experimental result has even suggested that Ti must diffuse in the bulk during the absorption/desorption cycling.¹¹ The role of Ti in lowering the hydrogen desorption is also unclear. Some studies have found that the improvement of the hydrogen cycling kinetics is due to surface-localized catalytic species,^{12,13} while others speculate about the effect of Ti in the bulk.⁶ The energetics of the preferential sites for Ti have been investigated theoretically.^{14,15} However, no calculations are available that determine the energy needed to remove a hydrogen atom from pure, as well as Ti doped, sodium alanate. Thus, theoretical studies are still required in order to fully understand

the role of Ti in lowering the hydrogen desorption temperature. It is necessary, for instance, to clarify the effect of Ti on the different contributions for the hydrogen binding energy and what is important in the design and synthesis of new light metal hydrides suitable for hydrogen storage.

In this letter, we provide a theoretical study of the role of Ti in diminishing the hydrogen binding energy in the crystalline sodium alanate (NaAlH_4). This effect is one of the main contributions which causes a decrease in the hydrogen desorption temperature. Using the state-of-the-art theoretical calculations, we show that Ti weakens the strength of the covalent bond between Al and H atoms, thus allowing the hydrogen to desorb at a lower temperature. Such bond weakening is shown by evaluating the electron localization function (ELF) (Ref. 16), as well as the electronic density of states (DOS) for both the intrinsic crystal and when a Na atom is replaced by a Ti. This result is further established by calculating the energies needed to remove a hydrogen atom from both the NaAlH_4 and Ti-doped NaAlH_4 . We have found that it is 4.0 eV for the former and 1.9 eV for the latter. In the following, we provide the details of our theoretical calculations and a discussion of our results.

In order to study the electronic structure and total energies, we constructed a $2 \times 2 \times 1$ supercell consisting of 96 atoms ($\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$). To model Ti substituted at the Na and Al sites, we have used the $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ and $\text{Na}_{16}(\text{Al}_{15}\text{Ti})\text{H}_{64}$ supercells, respectively. The hydrogen vacancies are modeled by the $\text{Na}_{16}\text{Al}_{16}\text{H}_{63}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{63}$ supercells. The calculations were carried out within the framework of generalized gradient approximation (GGA) to density functional theory (DFT) (Ref. 17) using projector augmented plane wave (PAW) method,¹⁸ as implemented in VASP code.¹⁹ We used a cutoff energy of 500 eV for the plane-wave basis. In all calculations, self-consistency was achieved with a tolerance in the total energy of 0.1 meV. The DOS were calculated by means of the modified tetrahedron method of Blöchl *et al.*²⁰ and the ELF were calculated according to Ref. 16. The geometry optimization has been done (ionic coordinates and c/a ratio) by minimizing the Hellmann–Feynman forces on the atoms and stresses on the supercell. The structures are

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fully optimized without any symmetry constraint. The calculated lattice constants $a=4.95$ Å and $c=10.89$ Å, as well as the Na–Al and Al–H distances of 3.50 Å and 1.64 Å in pure sodium alanate, compare very well with the corresponding experimental values of 4.98 Å, 11.15 Å, 3.52 Å, and 1.63 Å, respectively.

We first investigate the energetics of preferential sites for Ti atoms. It is done by evaluating the cohesive energy of the $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$, $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ and $\text{Na}_{16}(\text{Al}_{15}\text{Ti})\text{H}_{64}$ supercells. Such energy is defined as the total energy of the system minus the sum of individual energies of atoms. By setting the cohesive energy of pure alanate to zero, we found the values of -1.47 eV and -0.54 eV when Ti occupies the Na and Al sites, respectively. The negative signs mean that the Ti-doped (NaAlH_4) is more stable than the pure one. It should be pointed out that such a stability analysis is made by taking the isolated Ti, Na, and Al atoms as a reference. Furthermore, the Ti atoms prefer to replace the Na atoms, and this energy is 0.93 eV lower than that when Ti replaces the Al atoms. These results are in agreement with the calculations of Iniguez *et al.*^{15(a)} However, we should also point out that different conclusions can be reached about the site preference of Ti if one uses the cohesive energies of Na, Al, and Ti as a reference, as has been done by Lovvik *et al.*^{15(b)} However, the energies necessary to remove hydrogen following Ti doping are less, irrespective of whether Ti occupies the Na or the Al site. In addition, it is necessary to perform the surface total energy calculations before concluding if Ti would prefer to occupy the bulk sites. Such a study is in progress and the results will be reported in due course.

Next, we discuss the effect of Ti doping on the electronic structure of sodium alanate. We do this by comparing the ELF as well as the electronic DOS for $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ supercells. The ELF has been recognized as a powerful tool to visualize different types of bonding in solids and molecules.^{16,21,22} According to its definition, the ELF can assume values in the range of 0–1, where 1 corresponds to perfect localization and 0.5 to the case of uniform gas. In Fig. 1(a), we display the two-dimensional distribution of ELF on (001) plane, where the color bar runs from the lowest (dark blue) to the highest (red) values. One can observe the high ELF within the AlH_4^- unit which confirms the expected covalent bonding between H and Al atoms. The very low values of the ELF between AlH_4^- and Na^+ reflect its ionic bonding. When Ti replaces a Na atom, the ELF profile changes [see Fig. 1(b)]. One can see a more or less uniform distribution of ELF in the interstitial region between the Ti and AlH_4^- unit (with values in between 0.3 and 0.6). This is a typical picture of the metalliclike bonding.²² Such nature of Ti– AlH_4^- bond is because the ionization potential of Ti (6.83 eV) is higher than that of Na (5.13 eV), so it is energetically less favorable for Ti to transfer its electron to AlH_4^- as Na did. As a consequence, the nature of the Al–H bond is also changed. One can observe that the ELF in the interstitial region between Al and H (the ones that are nearest neighbors of Ti atom) is clearly diminished. This shows the weakening of the strength of covalent bonding between them. Indeed, the bonding shows metallic character and the hydrogen atoms nearest to Ti have weaker binding energy. They can, therefore, be desorbed at lower temperatures. Another consequence of this ELF profile modification is the distortion obtained for the AlH_4^- tetrahedral structure. Here, we have

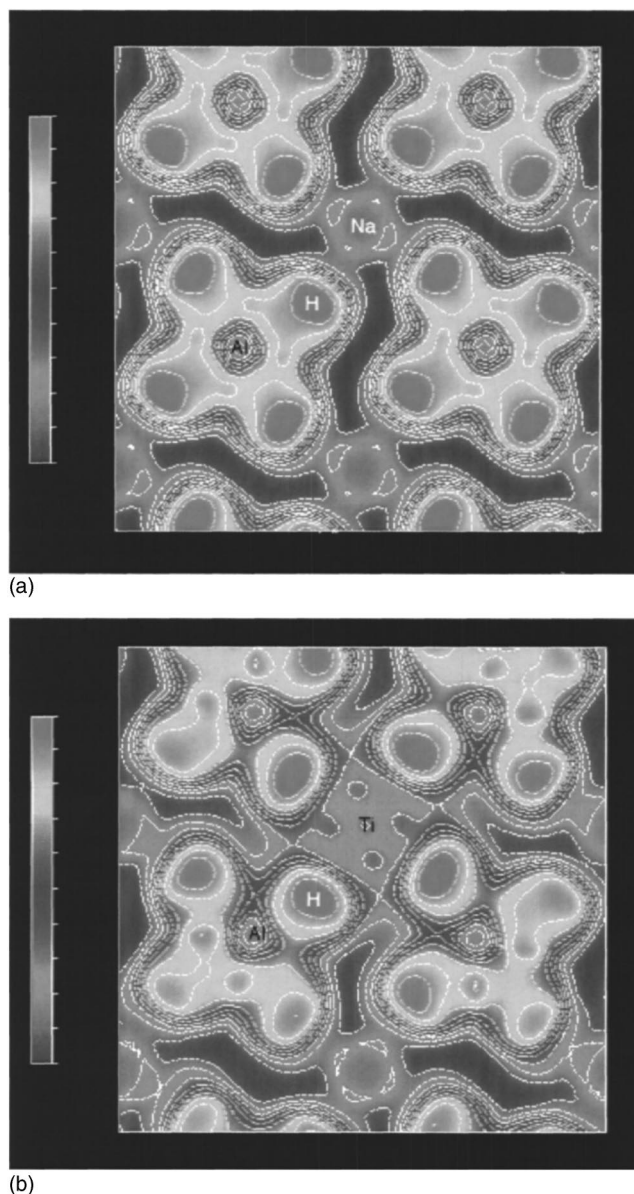


FIG. 1. (Color online) The two-dimensional distribution of ELF on (001) plane for both (a) $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and (b) $\text{TiNa}_{15}\text{Al}_{16}\text{H}_{64}$ supercells. The color bar runs from the lowest (dark blue) to the highest (red) values.

found that the Al–H bond length varies between 1.63 Å and 1.70 Å.

In Figs. 2(a)–2(h), we show the total and partial DOS for both the $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ supercells. The pristine sodium alanate is an insulator characterized by a band gap of nearly 5.0 eV. The uppermost region of the valence band (VB) is mainly composed by hybridization between H 1s and Al 3p states [see Figs. 2(c) and 2(d)], which is consistent with the covalent bond within the AlH_4^- unit. The bottom of the conduction band just above the Fermi level is formed primarily by Na s and p antibonding states [see Fig. 2(b)]. This is consistent with the ionic bonding between Na and AlH_4^- unit discussed above. As Ti replaces the Na site, Ti state appears in energy gap reducing the band gap and these states originate from Ti d states [see Fig. 2(f)]. This is consistent with the above finding that the bond between the Ti and AlH_4^- unit is not ionic. The effect on the Al–H bond can be seen in Figs. 2(g) and 2(h). Here, we have plotted the partial DOS for the Al and H atoms belonging to

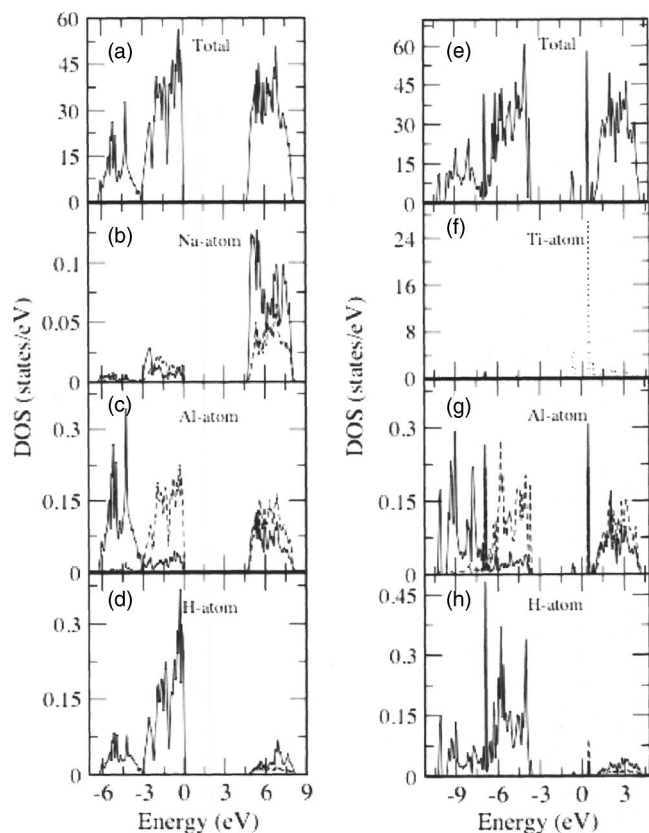


FIG. 2. The total and partial DOS for both $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ (panels a–d) and $\text{TiNa}_{15}\text{Al}_{16}\text{H}_{64}$ (panels e–h). The solid, dashed, and dotted lines represent *s*, *p*, and *d* states, respectively. The Fermi energy is set at zero energy.

AlH_4 unit that is nearest neighbor of the Ti atom. One can see that the uppermost region of the VB is still formed principally by hybridized H 1*s* and Al 3*p* states, however the DOS shape is clearly modified, which is a consequence of the electronic redistribution induced by Ti doping.

The change of Al–H bonding from covalent to metallic character resulting from Ti substitution permits the hydrogen to desorb at a lower temperature. This picture can be further established by calculating the energy needed to remove a hydrogen atom from $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ supercells. We have, therefore, computed the cohesive energies of $\text{Na}_{16}\text{Al}_{16}\text{H}_{63}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{63}$ supercells in which one of the hydrogen atoms bound to Ti and its equivalent atom bound to Na were, respectively, removed. The supercells again were fully optimized as discussed previously. The energies needed to remove a H atom from $\text{Na}_{16}\text{Al}_{16}\text{H}_{64}$ and $(\text{Na}_{15}\text{Ti})\text{Al}_{16}\text{H}_{64}$ supercells are, respectively, 4.0 eV and 1.9 eV. This confirms that Ti doping does weaken the Al–H bond.

In summary, we have investigated theoretically the effect of Ti doping on the hydrogen bonding in crystalline sodium alanate within the framework of GGA to DFT and using the PAW method. The calculated ELF and the electronic DOS give the same conclusion. The pristine sodium alanate is an

insulator where the hydrogen is bonded to Al covalently and Na and AlH_4 units are bound ionically. As Ti replaces the Na site, the strength of the covalent bond between Al–H is weakened and this is what results in a lower hydrogen binding energy. As a consequence, they can be desorbed at a lower temperature. The reason why Ti weakens the Al–H bond strength is that the ionization potential of Ti (6.83 eV) is higher than that of Na (5.13 eV). Thus, the bonding between Ti and AlH_4 unit is weaker than that between Na and AlH_4 as it is energetically less favorable for Ti to transfer its electron to AlH_4 as Na did. Thus, one can lower the desorption temperature by weakening the Al–H bond. This result is further confirmed by calculating the energy needed to remove one hydrogen atom from both the intrinsic and Ti-doped sodium alanate. We have found that it costs 4.0 eV for the former, whereas it costs only 1.9 eV for the latter.

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²See ([http://www.sc.doe.gov/bes/Basic Research Needs To Assure A Secure Energy Future FEB2003.pdf](http://www.sc.doe.gov/bes/Basic%20Research%20Needs%20To%20Assure%20A%20Secure%20Energy%20Future%20FEB2003.pdf))

³See the report of DOE Workshop on hydrogen in (<http://www.sc.doe.gov/bes/hydrogen.pdf>)

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