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Hydrogen-related defects in sodium alanate

A. Peles[*], C.G. Van de Walle

Materials Department, University of California, Santa Barbara, CA 93106-5050, USA

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Abstract

We present first-principles simulations to elucidate the role of hydrogen-related point defects in the hydrogen absorption/desorption processes in sodium alanate. In particular, we investigate the energetics and structural properties of crystal imperfections caused by addition or removal of hydrogen atoms. We specifically take the various charge states of the defects into account. We find that charged hydrogen-related defects are energetically more favorable than neutral defects; these systems have a negative effective correlation energy *U*. Significant local lattice relaxations are involved in stabilizing the hydrogen-related defects.

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1. Introduction

Hydrogen is actively being studied as an energy carrier for sustainable and clean energy consumption; however, the storage of hydrogen for mobile and portable applications remains a challenge [1,2]. Sodium alanate is considered a viable hydrogen storing system in which chemically bonded hydrogen can be stored or released through reversible chemical reactions, with the help of a small amount of transition metal (Ti, Zr, etc.). The addition of the transition metal speeds up uptake and release of hydrogen, and renders the process reversible [3]. Sodium alanate has a high gravimetric capacity of hydrogen (7.4 wt.%), but a theoretical value of only 5.6 wt.% is attainable at temperatures that are low enough for practical applications. The hydrogen uptake and release proceeds through the following sequence of reversible reactions

$$\mathrm{NaAlH_4} \rightarrow \frac{1}{3}\mathrm{Na_3AlH_6} + \frac{2}{3}\mathrm{Al} + \mathrm{H_2}\uparrow \quad (3.7\%),$$

$$\mathrm{Na_3AlH_6} \rightarrow 3\mathrm{NaH} + \mathrm{Al} + \frac{3}{2}\mathrm{H_2}\uparrow \quad (1.9\%),$$

$$\mathrm{NaH} \rightarrow \mathrm{Na} + \frac{1}{2}\mathrm{H_2}\uparrow \quad (1.8\%).$$

In order to address the issues of hydrogen uptake and release, we perform first-principles calculations of hydrogen-related defects in $\mathrm{NaAlH_4}$. The defects include a hydrogen vacancy, formed by removing a hydrogen atom from the lattice and leaving a dangling bond on aluminum, and a hydrogen interstitial, formed by adding an additional hydrogen atom to the lattice. These defects introduce additional energy levels in the band structure of the host material; it is therefore essential to take the various charge states of the defects into account.

2. Methods

We employ a first-principles approach based on density-functional theory (DFT) [4,5] and the projector augmented wave (PAW) method [6]. PAW potentials with valence states $2p^6$ and $3s^1$ for Na, $3s^2$ and $3p^1$ for Al, and $1s^1$ for H were used, as implemented in the VASP ab-initio simulation package [7]. The exchange-correlation energy was evaluated using the generalized gradient approximation (GGA) [8,9]. An energy cutoff of 450 eV was used for the plane-wave basis set. The Brillouin zone was sampled using a Monkhorst-Pack sampling technique [10], and a shifted 2 × 2 × 2 grid was found sufficient for a 96-atom supercell.

The structures and energies of the point defects are calculated in two steps. First, the equilibrium structure and total energy of the perfect crystal in a supercell geometry is determined. Then the point defect is introduced into an otherwise perfect lattice represented by a 96-atom supercell. The ionic positions are optimized using Helmann–Fynman forces in a conjugate-gradient algorithm until the absolute value of the force on each ion is less than 0.001 eV/Å. The formation energy of a defect, i.e., the energy cost to introduce the defect into a perfect lattice is calculated using the following expression [11,12]

$$E^{\mathrm{f}} = E_{\mathrm{tot}}(D^q) - E_{\mathrm{tot}}(\mathrm{bulk}) \pm \mu_{\mathrm{H}} + qE_{\mathrm{F}}, \quad (1)$$

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[*] Corresponding author. Tel.: +1 805 893 7499.

E-mail addresses: apeles@engineering.ucsb.edu (A. Peles), vandewalle@mrl.ucsb.edu (C.G. Van de Walle).

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where the first and second term are the total energies of supercells containing the defect and without the defect, respectively. μ_{H} is the chemical potential of hydrogen which (at $T = 0$) we fix to half of the energy of an H_2 molecule. The sign of the μ_{H} term is positive if hydrogen vacancy is created, and negative in case an interstitial is created. The last term in Eq. (1) relates to charged defects; q is charge of the defect and E_{F} is energy of the reservoir with which these charges are exchanged, i.e., the electron chemical potential or Fermi level. The shift in the reference level of the average electrostatic potential between the bulk and the supercell containing a defect was taken into account by explicit alignment of the potential [11]. The equilibrium concentration c of a defect at a given temperature T depends on the formation energy of the defect E^{f} and on the number of sites N on which the defect can be incorporated into the lattice:

$$c = N\,\exp\left(\frac{-E^{\mathrm{f}}}{kT}\right). \tag{2}$$

3. Results and discussions

$NaAlH_4$ is an insulator with a calculated band gap E_{g} of 4.75 eV. An experimental value of the band gap is not available. The calculated E_{g} value compares well with other DFT-based calculations [13,14], which are known to underestimate the band gap. A quasi-particle correction to the DFT value yields an E_{g} value of 6.9 eV [13]. The formation energies of a hydrogen vacancy in all possible charge states are plotted in Fig. 1 as a function of the position of the Fermi level in the band gap. The zero of Fermi energy is set at the valence-band maximum. The energy of a neutral vacancy V_{H}^{0} is higher than the energies of charged vacancies for any position of the Fermi level in the gap. This indicates that V_{H}^{0} is unstable and will decay into charged vacancies. Such behavior is characteristic of systems with a negative correlation energy U, and usually occurs in conjunction with significant lattice relaxations [15]. The gain in energy due to the local rearrangements in the lattice is illustrated in Fig. 1, where we plot both the formation energy of V_{H}^{+} without any lattice relaxation (dashed line) and that of the relaxed configuration (solid line). The relaxed geometry of the hydrogen vacancy V_{H}^{+} is shown in Fig. 2. In the perfect lattice, Na^+ ions and $AlH_4{}^-$ tetrahedral complexes occupy sites of tetrahedral symmetry in a crystal with the $I4_1/a$ space group [16] The presence of a vacancy, V_{H}^{+}, introduces large rearrangements of the surrounding lattice. In Fig. 2 the site where the hydrogen atom was removed from the lattice is marked by an open circle. The Al atom which was left with three neighboring H atoms when the vacancy was introduced moves toward the neighboring AlH_4 complex, partially attracting one of its hydrogen atoms, and resulting in the formation of a second AlH_3 complex with planar geometry. Note that among the possible AlH_n complexes AlH_3 is the most stable one.

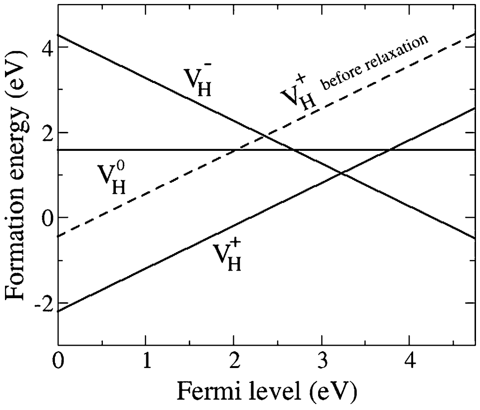

Fig. 1. Formation energies of the various charge states of the hydrogen vacancy as a function of Fermi energy E_{F}. The formation energy of V_{H}^{+} before structural relaxations are allowed is indicated by the dashed line.

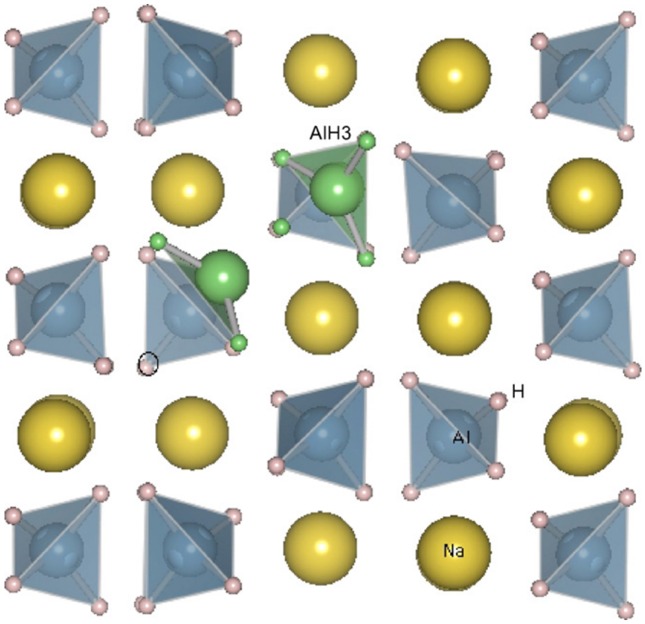

Fig. 2. Local atomic configuration around a hydrogen vacancy V_{H}^{+}. The open circle indicates the position of the site where a hydrogen atom is removed, creating the vacancy.

Turning now to the hydrogen interstitial, for each charge state we again systematically search for the minimum-energy structure. We place the additional hydrogen atom at different sites in the lattice (including high-symmetry sites but also sites lacking any symmetry) and perform structural optimizations in order to identify stable and metastable sites for the interstitial. Similar to the case of the hydrogen vacancy, the positive and negative charge states of the hydrogen interstitial ($H_i{}^+$ and $H_i{}^-$) have lower formation energies than the neutral interstitial $H_i{}^0$ for all possible values of the Fermi energy. The system therefore has a negative effective correlation energy U. The formation energies for interstitial hydrogen as a function of Fermi energy are shown in Fig. 3. A dramatic structural relaxation results from the presence of a hydrogen interstitial $H_i{}^+$ in the lattice, as shown in Fig. 4. The interstitial attracts a hydrogen atom from one of the AlH_4 complexes and forms an H_2 molecule, leaving a positively charged vacancy behind. The structural relaxation characteristic of the V_{H}^{+} defect, i.e., the formation of planar AlH_3 complex, is evident in figure.

At finite temperatures a crystal will contain concentrations of different types of defects. These concentrations are determined by the formation energies, as expressed by Eqs. (1) and (2). We have calculated the formation energies of metal-site related defects and find them to be quite high, much higher than those of the hydrogen-related defects. For example, the formation energy of neutral Na and Al vacancies are 3.87 eV and 5.53 eV, respec-

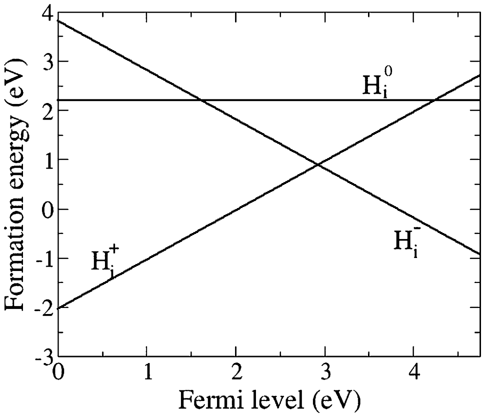

Fig. 3. Formation energies of the various charge states of the hydrogen interstitial as a function of Fermi energy E_F.

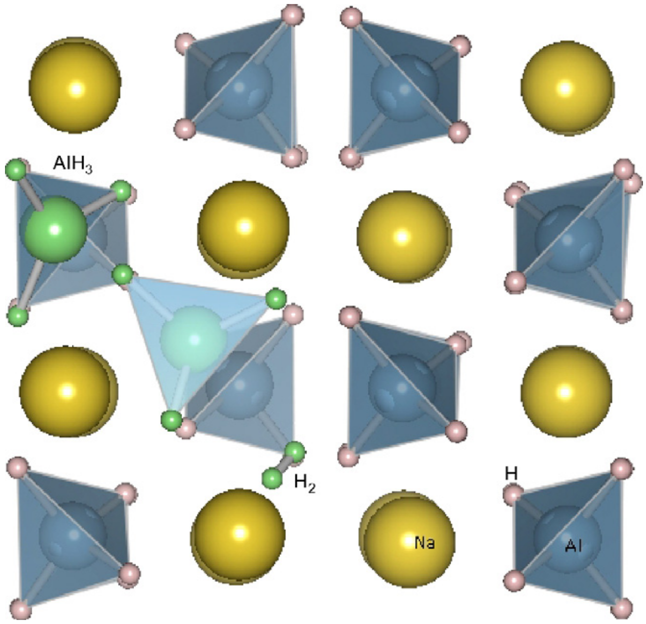

Fig. 4. Local atomic configuration around a hydrogen interstitial H_i^+. The resulting equilibrium structure consists of an H_2 molecule plus a vacancy V_H^+.

tively. This suggests that hydrogen-related defects are present in much higher concentrations. These findings are in agreement with recent anelastic spectroscopy experiments which suggest that a highly mobile point defect involving hydrogen is present at the temperature where decomposition of sodium alanate occurs [17].

4. Conclusions

We have presented a detailed study of the energetics and structural properties of hydrogen-related defects in $NaAlH_4$. Our results suggest that both the hydrogen vacancy V_H and the hydrogen interstitial H_i have negative correlation energies. Neutral V_H and H_i are unstable, and have lower energies in positive or negative charge states. Their formation energy depend on the position of the Fermi level in the band gap. Large structural relaxations are involved in stabilizing these defects. Our results for defect mobility and the role of transition metals in hydrogen uptake and release will be reported elsewhere.

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