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Hydrogen solution in tetrahedral or octahedral interstitial sites in Al

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ABSTRACT

It is reported that H atoms prefer to stay at interstitial (defect) sites with larger space in most metals. However, H atom prefers to occupy tetrahedral interstitial sites (T-site) that provide smaller space than octahedral sites (O-site) in Al. This paper studied the H–Al interactions from first principles calculations. Through analysis of the H-induced electronic states and the local atomic relaxations, we show that H–Al bonding interaction is stronger for T-site H, which is in favor of the solution energy. On the other hand, larger local atomic distortion is observed around the T-site H, which increases the total energy.

1. Introduction

The interaction between hydrogen and metal is one of the most important topics in materials physics, having broad range of technological implications. The bonding of H with metals determines the H storage capacity and desorption rate of H_2 from the metal hydrides [1,2]. In the process of production of H_2 via metal catalyzed chemical reactions, the H–metal interaction plays an important role [3]. Despite many years of research, some fundamental aspects underlying the H–metal interaction remains poorly understood because of the complex nature of this interaction.

H–metal interaction is also relevant to the H embrittlement. In recent years, a number of first principles studies have investigated the H embrittlement. Lu and Kaxiras have found that vacancies play crucial role in H embrittlement of Al [4], and Liu et al. also emphasis the role of vacancies in W [5]. In both cases, it is found that H prefers locating at tetrahedral sites (T-sites). According to Liu et al., H prefers to site at T sites in body centered cubic (BCC) W because T-sites provides more space to accommodate H atom, and this interstitial space determined site preference idea applies correctly to many other BCC metals such as group V transition metals [6]. This idea is also confirmed by other face centered cubic (FCC) metals such as Cu and Pd [7], in which H prefers to take octahedral sites (O-sites) since O-sites provides more space in FCC structures. However, this idea is not true for the case of FCC Al. In Al, although O-sites provide more spaces for H accommodation, H prefers to take T sites.

As mentioned above, the H embrittlement is always relevant to the formation of vacancies, in which H may accumulate since vacancies provide large amount of space. On the other hand, vacancy reduces charge density in its vicinity to provide an isosurface for collective H binding, causing H segregation and hence H bubble nucleation when H density reaches a critical density on the internal vacancy surface [5]. Obviously, the mechanism on the vacancy assisted H embrittlement is strongly related with the assumption that H prefers to stay at places with more spaces (interstitials sites or vacancies).

In the present work, we present systematic studies on H–Al interaction, we demonstrate the H occupying T-site is more stable than O-site, trying to understand the intrinsic physics concerning the "abnormal" behavior of H dissolution in FCC Al lattice.

2. Computational details

Calculations are done within the plane-wave pseudopotential method and density functional theory (DFT), which are imple-

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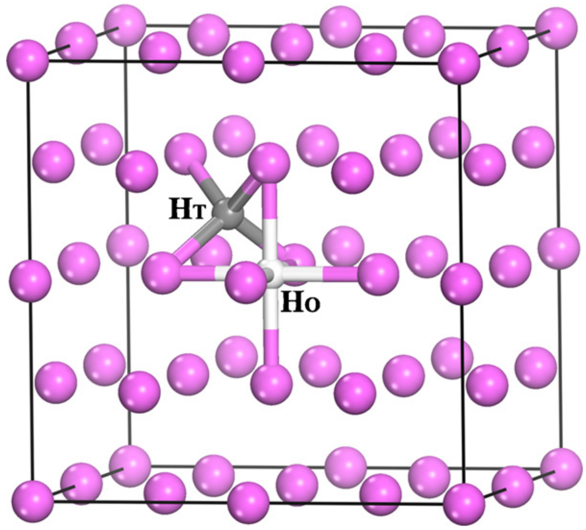

Fig. 1. Schematic view of the octahedral and tetrahedral H atoms in FCC Al. Large (purples) and small (grey for H_T and white for H_O) balls are Al and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

mented in the Vienna ab initio simulation package (VASP) [8,9]. The core ion and valence electron interaction is described by the projector augmented-wave method (PAW) [10], while the exchange–correlation part is described with generalized gradient approximation (GGA) by Perdew and Wang [11]. The convergence tests of the total energy with respect to the K-points sampling have been carefully examined. A 2 × 2 × 2 supercell is used for the Al metal system and a Monkhorst–Pack [12] scheme of 5 × 5 × 5 K-point mesh is used for the K-points sampling within the Brillouin zone. Energy cut-off for the plane waves is chosen to be 300 eV. Before the calculation of the electronic structure, all the atomic positions and lattice parameters are fully relaxed and the final forces on all relaxed atoms are less than 0.005 eV/Å. The Methfessel–Paxton smearing method [13] with $N = 1$ and $\sigma = 0.2$ eV is used in all calculations to treat metallic systems.

3. Results and discussion

Fig. 1 shows schematically the octahedral and tetrahedral H atoms in the Al 2 × 2 × 2 supercell. The optimized lattice constant of FCC Al is 4.0495 Å, which agrees well with the experimental date 4.049 Å [14]. Using this lattice constant and taking into account that atoms are closely packed along the ⟨1 1 0⟩ direction in the FCC lattice, the “radii” of the T-sites and O-sites are 0.32 Å and 0.59 Å, respectively. H_2 molecule has a covalent radius of 0.37 Å, which is slightly larger than the radii of T-sites and much small than the radii of O-sites. When we examine the details of the relaxed structures of $Al_{32}H$, we find that the cell shape remains unchanged and only the nearest neighboring (NN) Al atoms to the H atom move outwards by 0.13 Å and 0.04 Å when H is present in the T-site and O-site, respectively (refer to Table 1). The volume expansion of the supercell is *c.a.* 0.71% and 0.37% for H at T- and O-site cases, respectively. Very clearly, those data show that H atom at T-site repels its NN Al atoms more than at O-site, indicating that NN Al atoms interact much strongly with T-site H.

Table 2
Solution energies of H in dilute limit in different metals. The superscript “ZPE” denotes that zero point energy is included in the calculations.

	Solution energy (eV/H)		
	T interstitial site	O interstitial site	$E_{sol}(O) - E_{sol}(T)$
Al (FCC)	0.69 (0.68[a])	0.77 (0.77[a])	0.08 (0.09[a])
Al (BCC)	−0.02	0.38	0.40
Pd (FCC)	−0.02^{ZPE} [b]	−0.16^{ZPE} [b]	0.14^{ZPE} [b]
V (BCC)	−0.32[c]	−0.17[c]	0.15[c]
Fe (BCC)	0.20[d]	0.33[d]	0.13[d]

[a] Ref. [15].
[b] Ref. [16].
[c] Ref. [6].
[d] Ref. [7].

The interaction of interstitial H and host metal atoms can be studied by the solution energy, which is defined as $E_{sol} = E[\text{Metal} + \text{H}] - E[\text{Metal}] - \frac{1}{2}E[H_2]$, where $E[\text{Metal} + \text{H}]$, $E[\text{Metal}]$, and $E[H_2]$ are calculated total energies of the metal with one interstitial H atom, pure metal, and H_2 molecule in vacuum, respectively. The results are summarized in Table 2, in which solution energies of other BCC and FCC metals are also presented for comparison. As it is shown in Table 2, the tetrahedral interstitial site in FCC Al is slightly more favorable than the octahedral interstitial site by 0.08 eV. For all other cases listed in Table 2, H prefers to take T-sites in BCC lattice while O-sites in FCC lattice. As far as we know, for any other metals that we did not listed in Table 2, the H site preference is the same. Based on this point, we may think it could be interesting to know the site preference in the unstable BCC Al. Therefore, we calculate the solution energies and we found that H prefers to take T-site in BCC Al. The lattice constant of the BCC structure is chosen to be 3.214 Å, with which the mass density of the BCC Al is the same as the FCC Al. Then, if we take into account that Al atoms are closely packed along the ⟨1 1 1⟩ direction in the BCC structure, the radii of the T-site and O-site in BCC Al are 0.41 and 0.22 Å respectively. The space of T-site in BCC Al is large than that of FCC Al (0.32 Å) while the space of O-site in BCC Al is much small than FCC Al (0.59 Å). The calculated solution energies are −0.02 and 0.38 eV/H for T-sites and O-sites in BCC Al.

Now we discuss the electronic structure of Al–H system. Fig. 2 is the orbital projected density of states (PDOS) to Al atoms in Al_{32} and nearest neighboring (NN) Al atoms to H atom in $Al_{32}H_T$ and $Al_{32}H_O$. As it can be seen from Fig. 2, major differences are peaks at around −11.5 to −10.5 eV below the Fermi level. This difference is contributed by the so called H-induced states in the system. Because of the H–Al interaction, the Al-states (3p or 3s) at lowest energy ranges will form bonding and anti-bonding states with H-1s states. The bonding states will become lower in energy, and when the intensity of the interaction is stronger, the energy level of the bonding state is lower. In this sense, interstitials H in metal lattice pulls down part of the occupied metal states. As it is shown in Fig. 2(b) and c, the Al-3s and 3p states are pulled down by the H atom in both $Al_{32}H_T$ and $Al_{32}H_O$ cases, and the H-induced states are a little bit lower in energy level in the case of $Al_{32}H_T$, indicating that the H–Al interaction is a little bit more strong in $Al_{32}H_T$. We mention here that the PDOS of Al atoms far away from H atom in

Table 1
The lattice constant *a* and local atomic structure of $Al_{32}H_T$ and $Al_{32}H_O$.

	Unrelaxed		Relaxed		ΔV (%)	Δ*d* (%)
	a	d_{H-Al} (Å)	*a*	d_{H-Al} (Å)		
$Al_{32}H_T$	8.099	1.753	8.118	1.885	0.71	7.5
$Al_{32}H_O$	8.099	2.025	8.109	2.065	0.37	1.9

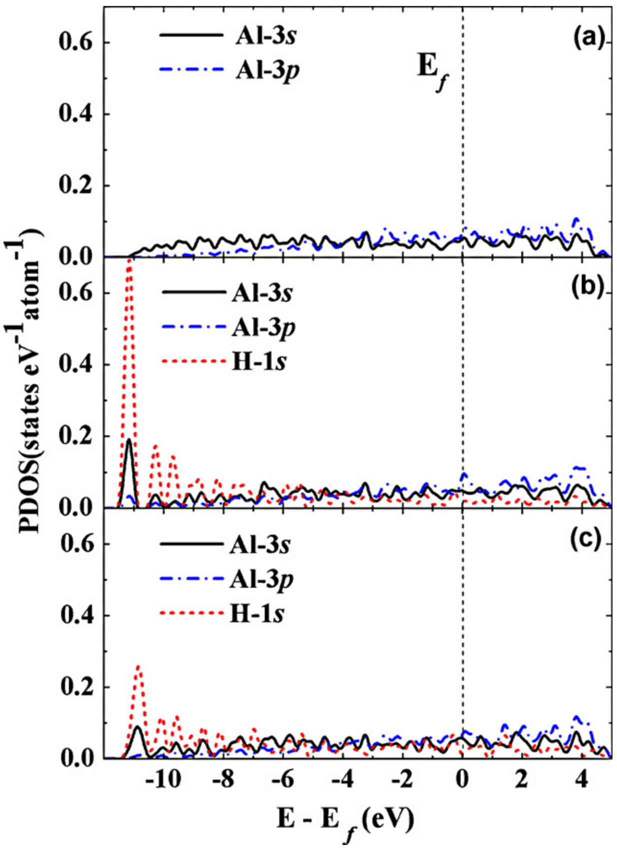

Fig. 2. Partial DOS of Al-3s (solid lines), Al-3p (dashed dot lines) and H-1s (short dashed lines) in (a) FCC aluminum, (b) FCC aluminum with T-site H, and (c) FCC aluminum with O-site H. In (b) and (c) the DOS is projected to nearest neighboring Al atoms to the interstitial H. The Fermi energy is set to 0 eV.

$Al_{32}H_T$ and $Al_{32}H_O$ do not change much, since interaction between those Al atoms and H is very weak.

More information on the H induced electronic states can be gained by comparing the band structures of Al_8H_T and Al_8H_O, as show in Fig. 3. Although these bands are quite similar for both Al_8H_T and Al_8H_O, very clear differences can also be observed in Fig. 3. From comparing of the lowest energy bands of Al_8H_T and Al_8H_O, we get the point that the energy levels of Al_8H_T in all high symmetric points are lower than that of Al_8H_O, which makes the total energy of the Al_8H_T system is lower than that of the Al_8H_O, as indicated by the solution energies discussed above.

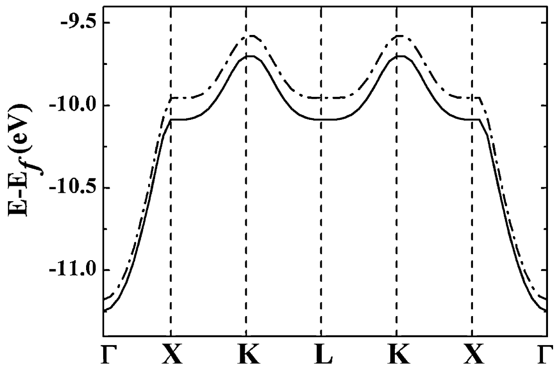

Fig. 3. Band structures of the H-induced states in Al_8H_T (solid line) and Al_8H_O (dashed-dot line). The Fermi-energy is set to 0 eV.

From the PDOS in Fig. 2, we also notice that the H-induced state is more confined in the H-1s sphere, since the main peak of the PDOS of the H-1s is much higher than Al-3s and 3p. Furthermore, the confinement of the H-induced state to H atom is clearer for the case of $Al_{32}H_T$ than that of $Al_{32}H_O$. This confinement effect can also be visualized from the charge density analysis, which provides possible observation of charge transfer and charge rearrangements upon hydrogen insertion into the metal lattice. Fig. 4 gives the differential charge density defined as $\rho_{diff} = \rho\,[Al_{32}H_{T/O}] - \rho\,[Al_{32}X_T]$, where $\rho\,[Al_{32}H_{T/O}]$ and $\rho\,[Al_{32}X_T]$ are charge densities of $Al_{32}H_{T/O}$ and the same structure without H atom, respectively. By this definition there is one net electron remaining in the 2 × 2 × 2 supercell. The majority of this net electron is localized around the H atom, with small portion located at nearby Al atoms. For the case of $Al_{32}H_O$, some very small amount of the charge is distributed at next-nearest neighboring (NNN) Al atoms. This is in agreement with the conclusion that the Al–H interaction in the case of $Al_{32}H_T$ is stronger than that of $Al_{32}H_O$, as discussed above.

From the above discussion, we may conclude that the "abnormal" H solution energy in T-site and O-sites of FCC Al is mainly attributed to the intensity of H–Al interaction. However, we still have no idea on why H–Al interaction is stronger when H locates at T-sites. As it is shown in Table 1, larger volume expansion and atomic relaxation occurred after H is put into the T-site, while much smaller relaxation effect is occurred in the case of $Al_{32}H_O$. This is clear since O site provides larger space for H. The radius of the O-site 0.59 Å is larger than the H covalent radius 0.37 Å. However, as the Al–H interaction is different from the H–H covalent bond, this covalent radius cannot apply directly here. On the other hand, figure out the Al–H equilibrium distance is more sensible. In order

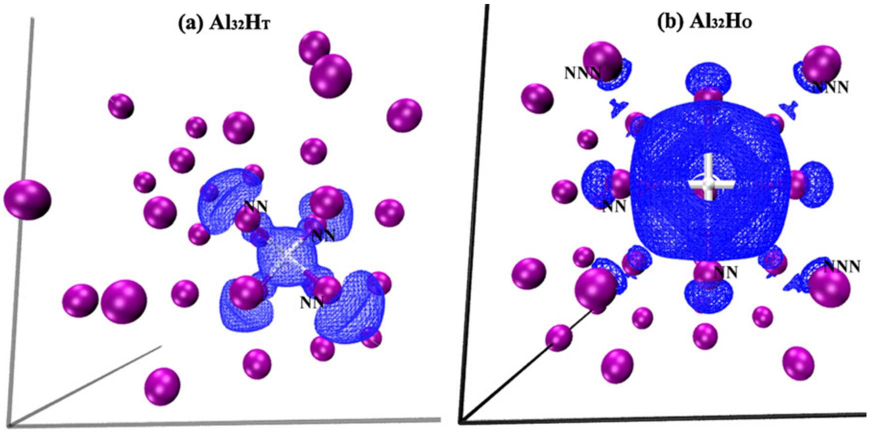

Fig. 4. The differential charge density of $\rho_{diff} = \rho[Al_{32}H] - \rho[Al_{32}]$ for (a) $Al_{32}H_T$ and (b) $Al_{32}H_O$. Large (purples) and small (white) spheres are Al and H atoms, respectively. NN and NNN denote nearest neighboring Al atoms and next-nearest neighboring Al atoms to H, respectively.

to obtain a reasonable Al–H equilibrium distance, Al cluster models are used in the present studies, because cluster models can release all constrains (confinements) of bulk Al atoms to H interstitials. We modeled a Al_4 cluster in tetrahedron geometry in an empty $15 \times 15 \times 15$ Å^3 cell, and H atom is placed outside of the tetrahedron. In this way, Al–H distance is freely relaxed and the equilibrium Al–H distance is 1.914 Å. This equilibrium distance is close to the Al–H distance in $Al_{32}H_T$ (1.885 Å) while smaller than the Al–H distance in $Al_{32}H_O$ (2.065 Å).

Now we understand that the "abnormal" H solution energy is related with the equilibrium Al–H distance. The Al–H interactions lower the total energy, while the deformation of the host Al lattice increases the total energy. The Al–H interaction for T-site H is stronger, which lowers the total energy. On the contrary, the small space of the T-site which induces much larger lattice deformation and in turn increases the total energy. As a result, although the H solution energy in T-site is lower than O-site, the difference is small (0.08 eV, see Table 2). On the other hand, in the case of BCC-Al, as the O-site is very small (Al–H distance is only 1.61 Å for O-sites while 1.80 Å for T-sites before relaxation), the deformation of the lattice is very large. Therefore, the solution energy at O-site is also higher than T-site.

4. Summary and conclusions

In summary, we have studied the structural, energy, and electronic aspects of the Al–H interactions by means of first-principles calculations. We demonstrated that the T interstitial site in Al is slightly more favorable for the H atom's occupancy than the O interstitial site, although O-site provides more space for H. On one side, the H-1s states and Al-3s and 3p states form bonding states upon H intercalation. This partly lowers the energy levels of the Al-3s and 3p states and in turn lowers the total energy of the system. We also showed the Al–H interaction is stronger when H is put into T-site, the energy levels of the H-induced states for T-site H atoms are lower than O-sites. The charge density analysis also confirmed this conclusion, as more charge is confined around the H atom in the case of $Al_{32}H_T$, indicating of stronger bonding is formed. On the other hand, as the T-site do not provide enough space to reach a Al–H equilibrium distance, NN Al atoms to the H atom relaxed outwards and the local atomic structure is deformed, which in turn increases the total energy. As a result, the H solution energy at T-sites is slightly lower than that of at O-sites.

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