POSITION OF HYDROGEN ATOM IN A VACANCY IN ALUMINUM METAL – AN *AB INITIO* STUDY

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Abstract. The optimal position of a hydrogen atom inside a vacancy in metallic aluminum has been studied using state-of-the-art density functional theory including generalized gradient correction. The bulk Al has been represented by a finite number metal atoms fixed at their bulk lattice positions. The hydrogen atom has been moved along various directions and for each position of the hydrogen atom the total energy of the system has been calculated. The resulting energy surface shows that the strong interaction of Al-H causes the hydrogen atom not to be at the center of the vacancy.

1. INTRODUCTION

The interaction of hydrogen with aluminum is interesting for technological reasons and the commercial exploitation of the associated technologies. However, in its own right this interaction is an interesting physical problem. For example, the implantation of hydrogen in aluminum can cause embrittlement. It is known to shift the superconducting transition temperature from 1.18K to 6.75K [1]. Hydrogen may accumulate in vacancies within aluminum and cause blistering. This is important to the electronics industry because electrical contacts with semi-conducting material are made using the chemical vapor deposition of aluminum. This is sometimes performed with the use of dimethylethylamine (alane) with hydrogen as the carrier gas. This may cause the adsorption of hydrogen on the surface of the deposited aluminum pads and the subsequent migration of hydrogen into subsurface regions. It has been shown that although hydrogen favors the tetrahedral site over the octahedral site [2] it is clearly established by calculations on the perfect crystal that these sites are unstable relative to the adsorption of hydrogen on the surface. Picraux [3] has showed that point defects called mono-vacancies are the most like trapping centers for subsurface hydrogen.

It has been observed that if a vacancy exists in aluminum in the presence of hydrogen, a hydrogen atom will diffuse towards the point defect to occupy it [3]. However, contrary to expectation, the hydrogen atom never occupies the exact position from which the aluminum atom was lost. It sits at an asymmetrical point instead, away from the exact position of the point defect. This behavior is not confined to hydrogen in aluminum. Rao *et al*. [4] have pointed out that hydrogen moves away from the most symmetric site of lithium clusters. For the current work, the plan is to perform an ab initio study of the interactions of a hydrogen atom trapped inside a vacancy in bulk aluminum.

2. CHOICE OF THE MODEL

The structure of bulk aluminum is face centered cubic (fcc). A small fragment of an fcc crystal is given in Fig. 1. In this figure, the nearest neighbors to any face-centered atom reside on three intersecting planes that are perpendicular to each other. At the point where the three planes intersect an atom exists. In this paper this site is referred to as the symmetric site. In this work, the thirteen aluminum at-

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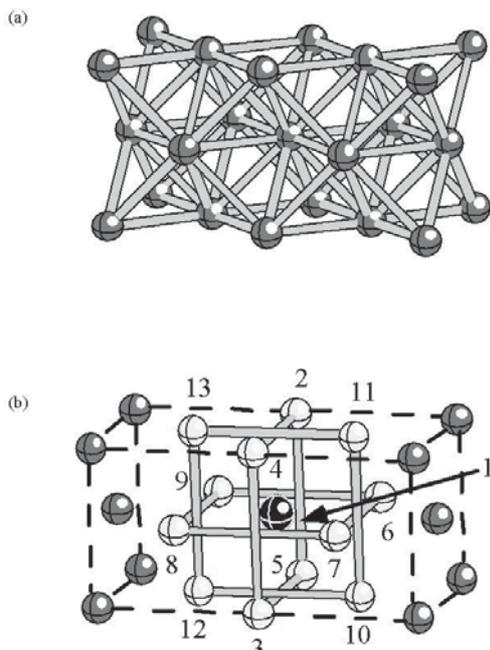Corresponding author: B.K. Rao, e-mail: bkrao@vcu.edu

Fig. 1. (a) Structure of the fcc lattice of bulk aluminum. (b) The 13 atoms chosen to represent bulk in this work are shown as the lighter shaded atoms.

Fig. 2. Coordinates determining the position of the hydrogen atom with respect to the center of the vacancy. The atomic numbers are as defined in Fig. 1.

oms used to model bulk aluminum are represented by lighter shade. Four atoms are placed at the corners of each intersecting plane and one atom is at the symmetric site. This figure shows the relationship of the atoms of the chosen model to the cell structure that makes up bulk aluminum. Note that four of the atoms are at the corners of the cells and lie on a plane between the two cells. The other nine atoms are face-centered atoms. The central aluminum atom and its twelve nearest neighbor are shown to lie on three intersecting planes. The numbers used to identify them in the model labels the atoms. These numbers will be used later while studying site dependent properties. As the atoms are placed at their corresponding bulk lattice sites and are kept unmoved during the calculation, this should be a reasonable representation of a bulk Al metal.

3. CALCULATIONS

To make the study as close to reality as possible, the central aluminum atom of the 13-atom cluster used to represent the bulk was removed to create a vacancy. Then a hydrogen atom was placed in this vacancy exactly at the position of the central Al atom that had been removed. Starting from this po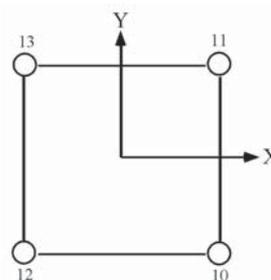sition, it was then moved along specific paths as described below. For each position of the hydrogen atom inside the vacancy, the total energy of the system was calculated using density functional theory [5-7] with gradient correction incorporated through Becke-Perdew-Wang (BPW91) scheme [8-10]. The LanL2DZ basis set [11] was used for the calculations. This basis uses the full double zeta Dunning/Huzinaga basis set [12] for the first row elements and Los Alamos effective core potential [13-15] plus double zeta split valence on elements from Sodium to Bismuth.

The calculated total energy of the $Al_{12}H$ where the H atom was placed at the center of the vacancy was used as the reference energy. Then the configurations were changed through changes in the location of the hydrogen atom within the vacancy. The configuration of the system was varied as follows. A plane passing through the center of the model was chosen (Fig. 2). The hydrogen atom was then moved to various positions on the plane and the total energy of the system was calculated for each position of the hydrogen atom. The points at which to locate the hydrogen atom were determined as follows. The fcc cell of aluminum has an edge length 4.0496 Å in the bulk. This value was maintained for our model. The distance from the center to the edge was divided into 16 parts. The hydrogen atom was moved in incremental steps of 0.12655 Å along the x-axis. After covering this distance, once again the same scanning was done but at an angle of 10° to the x-axis. Similar scans were repeated along lines that made angles of 20°, 30°, 40° and 45° with the x-axis. Using symmetry, the energies obtained for different points in this sector can provide information about the energies along the defined plane throughout the entire vacancy. In order to get a complete understanding of the energetics associated

Table 1. Total energy and charge at the site of the central atom for different positions of the central plane as it is being moved along the x-axis (Fig. 2).

| Distance from center (Å)	Charge at the central atom		Total energy (Hartree) with the central atom	
	Al	H	Al	H
0.0	-1.74	-0.2665	-26.1947	-24.6242
0.12655	-1.699	-0.2088	-26.1918	-24.6265
0.2531	-1.624	-0.2176	-26.1865	-24.6290
0.37965	-1.476	-0.2271	-26.1767	-24.6327
0.5062	-1.3211	-0.2351	-26.1636	-24.6369
0.63275	-1.1596	-0.2604	-26.1464	-24.6420
0.7593	-0.98734	-0.2713	-26.1246	-24.6483
0.88585	-0.8117	-0.2814	-26.0985	-24.6536
1.0124	-0.6346	-0.2916	-26.06897	-24.6579

with the position of hydrogen within the aluminum cell, we extended the investigation to include corresponding paths on planes that are parallel to the central plane. The planes chosen were 0.5 Å, 1.0 Å, 1.5 Å, and 2.0 Å from the central plane. This now allows a three dimensional picture of the energetics of the system to emerge.

4. RESULTS AND OBSERVATIONS

The total energies of Al_{13} and Al_{12} systems in the configurations defined here are -26.19467 Hartrees and -24.06407 Hartrees respectively. The energy of the Hydrogen and the Aluminum (frozen core) atoms are -0.49823 Hartree and -1.93962 Hartrees respectively. Defining the binding energy of any atom X with Al_{12} as $\Delta E = E(Al_{12}X) - E(Al_{12}) - E(X)$, we see that a negative value of ΔE represents a binding between Al_{12} and X. For our values here, ΔE is -5.19 eV for a binding between Al_{12} and Al. The total energy of $Al_{12}H$ with H at the center of the vacancy is -24.62420 Hartrees. Thus, ΔE for hydrogen is -1.68 eV. Clearly Al_{13} and $Al_{12}H$ are both bound systems. However, these systems behave differently in response to movement of the central atom away from the symmetric position. This contrast in behavior is shown in Fig. 3 when the central Al atom or the H atom is moved away from the center along the x-axis towards the edge (Fig. 2) of the central plane. The electronic charges associated with the central atom while it is being moved are given in Table 1 for Al and H.

Note that the total energy of Al_{13} rises, i.e. the system is less bound, as the distance of the aluminum atom from the center increases. This is expected as the central aluminum atom at the symmetric site is at a position for the bulk. On the other hand, for $Al_{12}H$ the total energy decreases when the hydrogen atom moves away from the center and the binding of the hydrogen to Al_{12} increases. This is in agreement with other observations [4], which show that the most likely place for hydrogen to sit in such a system is displaced from the center.
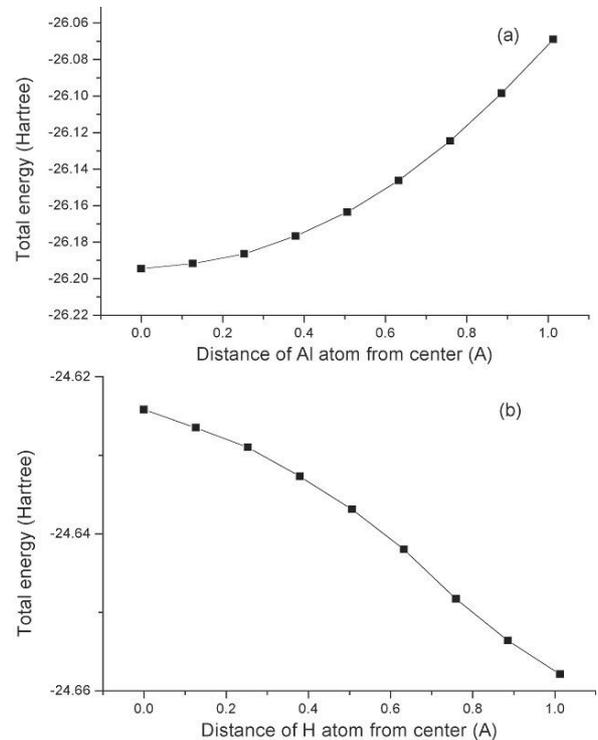
Fig. 3. Variation of the total energy of the system with the movement of the central (a) Al atom and (b) H atom along the x-axis (see Fig. 2).
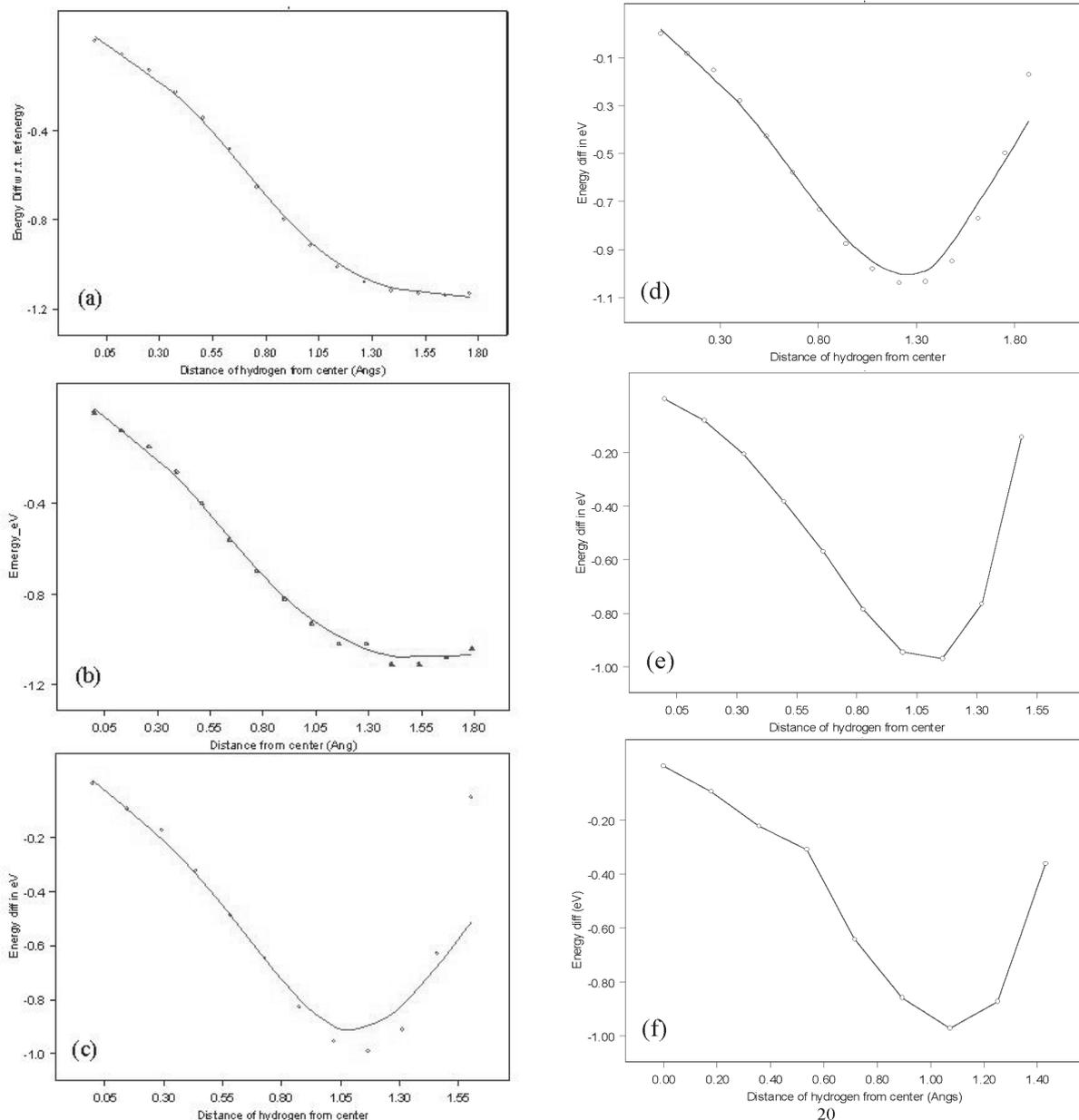
Fig. 4. Change in energy as hydrogen is moved in the central plane (see Fig. 2) along a line at an angle of (a) 0°, (b) 10°, (c) 20°, (d) 30°, (e) 40°, and (f) 45° to the x axis.

The graph in Fig. 3(b) shows that the energy of the system may decrease indefinitely with increase of distance from the center. This, however, is an artifact of the model as only a single cell was used. In practice, as the hydrogen atom approaches the edge of the cell, it comes under the influence of the adjacent cell and the energy of the system is expected to rise again as it approaches the edge of the adjacent cell. This reflects the periodic nature of bulk aluminum.

From Table 1 it is noticed that the system energy decreased and the charge on the hydrogen atom increased as the hydrogen atom moved fur-

ther from the center while the converse was true for the central aluminum atom. Rao *et al.* [4] have explained that the increase of charge on the hydrogen atom is due to symmetry breaking. This allows electronic states other than the s-states to contribute to the binding of the hydrogen atom.

As the next step we have investigated the variation of the energy of the $Al_{12}H$ system as a function of position of hydrogen along paths that are 0, 10, 20, 30, 40, and 45 degrees with respect to the x-axis. The results are presented in Fig. 4, the change in energy being calculated from the energy of $Al_{12}H$ with H at the center of the void. We see that in
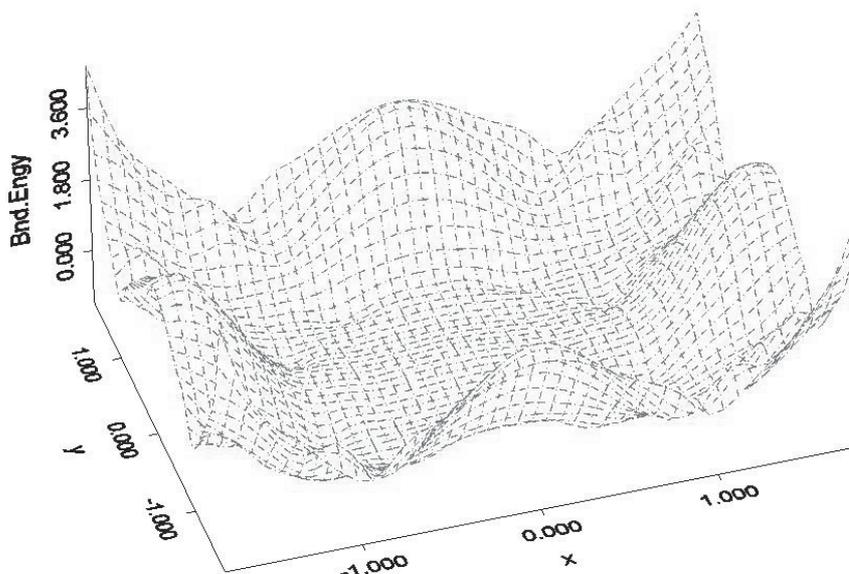
Fig. 5. Potential energy surface depicting the energy of a hydrogen atom in the central plane.

every instance the energy of the system decreases as the hydrogen atom is moved from the central location along the paths investigated. It also shows that as the path is rotated away from the x-axis the location of the minimum energy moves closer to the center and becomes shallower. The nearest minimum is along the path 45° to the x-axis. This occurs at 1.07Å from the center. As the angle changes from 0 to 45 degrees the chance of the hydrogen encountering an aluminum atom increases and at 45° if the H atom would keep on progressing along the line, it would come up against an Al atom (atom at position 11 in Fig. 2). This causes the in-

crease in energy producing the minimum closer to the center. The values of the lowering of the energy are provided as a function of angle in Table 2.

These results suggest that if the hydrogen atom is constrained to the central plane then the most likely place it will be found is on the x-axis 1.645 Å away from the center. This position is 2.06 Å away from the two closest edge atoms and has the least steric hindrance. The minima along the other paths occur at distances of 1.9 Å, 1.8 Å, 1.76 Å, and 1.79 Å from the nearest aluminum atom. These values are comparable to the bond length of the Al-H dimer, which is 1.66 Å – 1.70 Å.

Using the 8-fold symmetry of the problem, the result can now be extended to the rest of the central plane. When this is done the picture of an energy surface emerges with an irregular trough that encircles an elevated central region. The bottom of this trough is closest to the center of the cell at 1.07 Å along the line 45° to the x-axis and is as far away as 1.70 Å away from the center along the x-axis. The resulting potential energy surface is shown in Fig. 5.

In order to obtain a more complete understanding of the behavior of hydrogen in aluminum we examine its behavior on different planes through the cell. For each plane chosen, the hydrogen atom was constrained to move within that plane along the trajectories previously described for the central plane. The chosen planes were parallel to the central plane at distances of 0.5 Å, 1.0 Å, 1.5 Å, and 2.0 Å from the central plane. Obtaining this information would finally give us a complete view of the energet-

Table 2. The positions of the minima in the total energy of $Al_{12}H$ when the hydrogen atom moves away in the central plane in different directions. The corresponding change of the energy is also provided with respect to the reference energy (energy of $Al_{12}H$ with H at the center of the model).

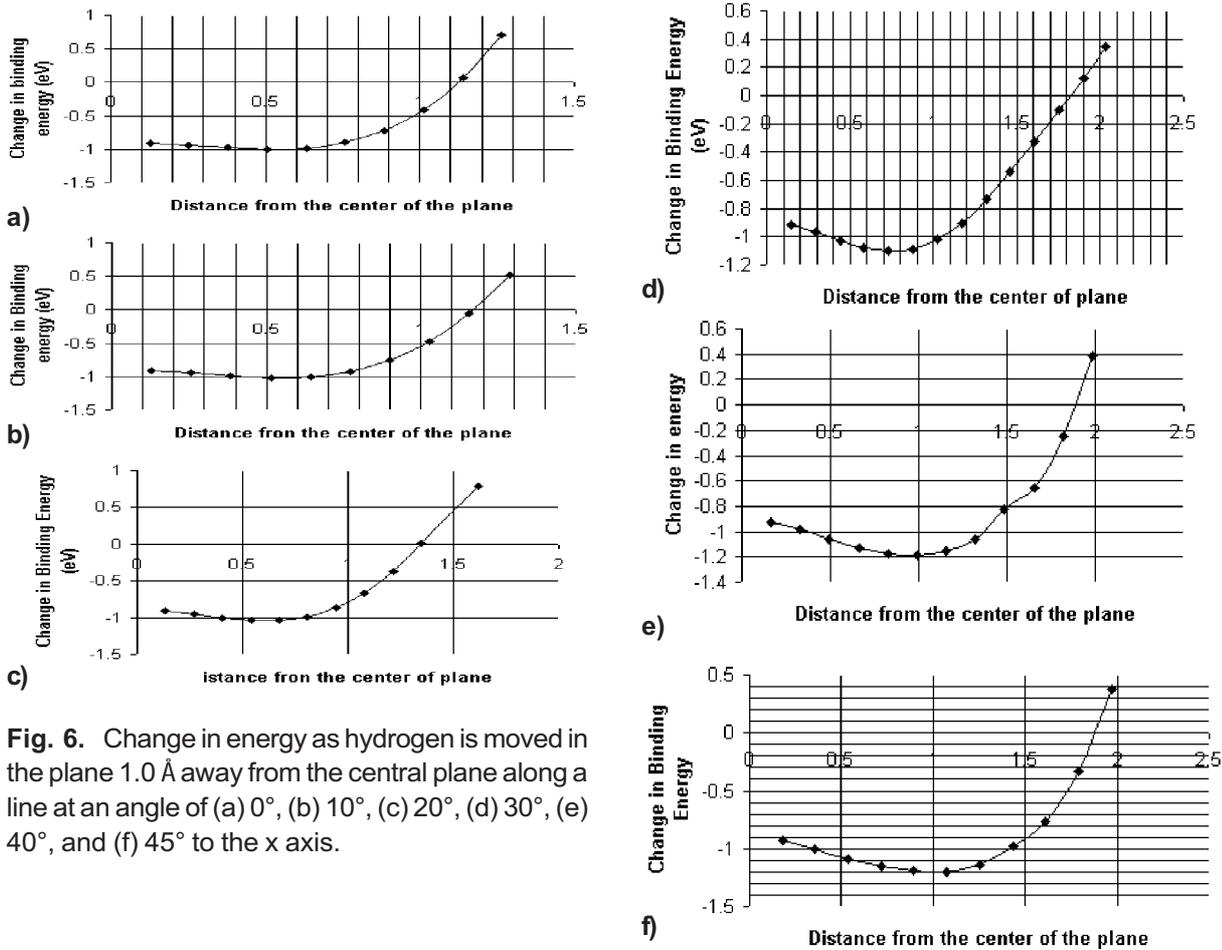| Angle	Distance of the minimum from the center (Å)	Change of energy (eV)
0°	1.645	1.14
10°	1.414	1.11
20°	1.212	1.04
30°	1.169	0.99
40°	1.156	0.97
45°	1.07	0.97

Fig. 6. Change in energy as hydrogen is moved in the plane 1.0 Å away from the central plane along a line at an angle of (a) 0°, (b) 10°, (c) 20°, (d) 30°, (e) 40°, and (f) 45° to the x axis.

ics experienced by the hydrogen atom inside the vacancy caused by the removal of the central aluminum atom.

On each plane we proceeded as previously described for the examination of the central plane. We calculated the energy of the system at different locations of the hydrogen atom along paths that make angles of 0.0°, 10.0°, 20.0°, 30.0°, 40.0°, and 45.0° to the x-axis in that plane. The results for the plane

at a distance of 1.0 Å from the central plane are given in Fig. 6. In this case, contrary to the observations at the central plane, the deepest minimum occurs along the path 45° to the x-axis. In fact, this minimum along the 45° path is the global minimum for the system.

Table 3 lists the distance of the minimum in each plane from its center ($R1$), the distance of the minimum in each plane from the center of the cell (R),

Table 3. The distance of the minimum in each plane from its center ($R1$), the distance of the minimum in each plane from the center of the cell (R), the angle of the path along which the minimum occurs, the binding energy with respect to hydrogen at the center of the cell, and the excess charge on the hydrogen atom for all the planes studied.

Plane Height (Å)	$R1$ (Å)	R (Å)	Angle	Energy (eV)	Charge on H
0.0	1.6452	1.6452	0.0°	-1.14	-0.326
0.5	1.0738	1.1845	45.08°	-1.169	-0.296
1.0	1.0738	1.4670	45.08°	-1.199	-0.321
1.5	0.1285	1.5055	10.08°	-1.153	-0.317
2.0	0.1285	2.004	10.08°	-1.107	-0.316

the angle of the path along which the minimum occurs, the binding energy with respect to hydrogen at the center of the cell, and the excess charge on the hydrogen atom. The deepest minimum is at a distance of 1.467 Å from the center of the cell. The hydrogen atom gains slight charge ($\approx$ -0.3). This is similar to H in metals [16] where the gain by H is approximately -0.4.

To answer the question where would a hydrogen atom sit in a cell with a point defect as described, we can now suggest with confidence that this atom will occupy a position 1.47 Å from the center at an angle of 45° to the x-axis and an azimuthal angle of 42.9°. Since there are six equivalent face centers in each cell each with the four-fold symmetry of the 45° path, there are twenty-three additional equivalent positions, which are just as likely to be occupied.

The best position corresponds to the bond length of the AlH dimer. In addition, the nearest aluminum atoms contribute to the excess charge on hydrogen. The other minima are not as deep and have longer hydrogen to aluminum distances. Finally, although there is a correlation between the excess charge on the hydrogen atom and the energy of the system, the distance between hydrogen and the nearest aluminum atoms is the most influential. This is supported by the fact that when hydrogen is at the central position the excess charge on hydrogen is 0.27 of an electron. This value is not exceeded until the hydrogen atom is displaced 0.76 Å from the center.

ACKNOWLEDGEMENTS

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