Parametrization of a reactive force field for aluminum hydride

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A reactive force field, REAXFF, for aluminum hydride has been developed based on density functional theory (DFT) derived data. REAXFFAlH3 is used to study the dynamics governing hydrogen desorption in AlH3. During the abstraction process of surface molecular hydrogen charge transfer is found to be well described by REAXFFAlH3. Results on heat of desorption versus cluster size show that there is a strong dependence of the heat of desorption on the particle size, which implies that nanostructuring enhances desorption process. In the gas phase, it was observed that small alane clusters agglomerated into a bigger cluster. After agglomeration molecular hydrogen was desorbed from the structure. This thermodynamically driven spontaneous agglomeration followed by desorption of molecular hydrogen provides a mechanism on how mobile alane clusters can facilitate the mass transport of aluminum atoms during the thermal decomposition of NaAlH4. © 2009 American Institute of Physics. [DOI: 10.1063/1.3182853]

I. INTRODUCTION

One of the major challenges in the quest for hydrogen storage solutions is the development of solid-state hydrogen storage media for vehicles. The United States’ Department of Energy (DoE) has set a minimum target of 6 wt % H2 for economically practical storage of hydrogen in a solid-state material by the year 2010. AlH3, which has about 10.1 wt % of H2 and a volumetric density of 0.148 kg H2/l, is quite attractive as a potential candidate for onboard hydrogen storage applications in proton exchange membrane fuel cells. AlH3 is a covalently bonded metastable binary hydride, with polymeric (AlH3)n forms. There are at least seven (α, α′, β, γ, δ, ε, and ζ) known nonsolvated phases of AlH3.1,2 Experimentally, under ambient conditions, the most stable phase of AlH3 is α-AlH3, which has a trigonal/rhombohedral crystal structure (space group R3c) with lattice parameters a =4.449 Å and c=11.804 Å.3 The basic building unit of all the AlH3 polymorphs is the AlH6 octahedra and the α-AlH3 polymorphic modification is the most densely packed. In 2005, Ke et al.,4 using density functional theory (DFT), identified two structures of AlH3 (cubic Fd3m and orthorhombic Cmcm), which were theoretically calculated to be more stable than α-AlH3. In 2006, the Institute for Energy Technology (IFe) experimentally solved the structure of orthorhombic α′-AlH3. In the same year, a joint collaboration of University of Hawaii (UH), IFE, and Brookhaven National Laboratory (BNL) synthesized and solved the structures of cubic Fd3m (β-AlH3) and tetragonal P4mm (γ-AlH3) using organometallic methods.5 All the three structures were found to be less stable than α-AlH3 at temperatures over 300 K.

The metastable AlH3 does not release hydrogen under ambient conditions of temperature and pressure. Although all the known AlH3 phases are thermodynamically unstable with an equilibrium decomposition pressure in the range of kilobars at room temperature, they are usually metastable and slowly decompose at room temperature. The cause of this metastability is the encapsulation of the hydrogen in AlH3 by a layer of Al2O3 that surrounds the surface of the AlH3 particles. At atmospheric pressure and in the temperature range of 330–400 K, subject to its preparation history, the decomposition of AlH3 occurs in a single step as follows:

\[
\text{AlH}_3 \rightarrow \text{Al} + \frac{3}{2} \text{H}_2. \tag{1}
\]

Thermodynamically, this reaction is not easily reversible. To rehydrate Al back to AlH3 hydrogen gas pressures of over 2.5 GPa are needed.6,7 AlH3 has a low decomposition enthalpy of about 1.82 kcal/mol H2,8 which is 20% that of NaAlH4.9 The decomposition rate of AlH3 can be tuned through nanostructuring (particle size reduction).5 However, the decomposition reaction of AlH3 is not reversible and therefore the desorbed hydrogen must be regenerated off-board. There are various ongoing research efforts to improve the sorption kinetics of AlH3. Sandrock et al. have shown that doping of AlH3 with small amounts of alkali metal hydrides (LiH, NaH, and KH) leads to accelerated H2 desorption rates at low temperatures.10,11
In this work we have parametrized a reactive force field (REAXFFAlH₃) for AlH₃ with the objective of describing the H₂ desorption process in AlH₃. REAXFF has already been shown to be able to accurately predict the dynamical and reactive processes in hydrocarbons, silicon/silicon oxides, aluminum/aluminum oxides, nitramines, sodium hydride, and magnesium hydride. Herein, the details of the parametrizations of REAXFFAlH₃, the diffusion mechanism of hydrogen atoms and hydrogen molecules in AlH₃, the abstraction process of surface molecular H₂ in AlH₃ cluster, the possibility of phase transition between different polymorphic modifications during the heating process, and the role of alane clusters in the transportation of Al atoms are examined. In addition, interestingly, this paper shows that small alane molecules have to first of all agglomerate before desorption of molecular hydrogen can occur. This is very important in understanding the mass transport of aluminum and sodium alanes in AlH₃. We conclude in Sec. VI.

This paper is organized as follows. Section II deals with force field parametrizations and the tests taken to ensure that the force field is well parametrized. Sec. III deals with the dynamics of hydrogen desorption in aluminum hydride clusters and the behavior of alanes on Al(111) surface. Sec. IV focuses on the abstraction process of molecular hydrogen from a cluster of AlH₃ and Sec. V is devoted to the issue of trapped molecular hydrogen in the channels of a cluster of AlH₃. We conclude in Sec. VI.

II. FORCE FIELD PARAMETRIZATIONS

REAXFFAlH₃ has been parametrized in the same way as REAXFFNaH (Ref. 17) and REAXFFMgH. The force field does not use fixed connectivity assignment between atoms but rather the bond-order formalism, which allows for bonds to be created and broken-up in line with the works of Tersoff and Brenner. REAXFF calculates nonbonded (van der Waals and Coulomb) interactions between all atoms (including 1–2, 1–3, and 1–4 interactions) making it suitable for systems which have polar-covalent interactions. Implemented in REAXFF are polarizable charges that are calculated using electronegativity equalization method (EEM) and which provides a geometry dependent charge distribution.

The fitting data used in REAXFF were obtained from DFT using the efficient and accurate total-energy package, VASP (Vienna ab initio simulation package). VASP implements a projector augmented plane-wave (PAW) approach. In determining the relaxed geometries of the structures considered in this work, a plane-wave cutoff of 600 eV (1 eV = 23.06 kcal/mol) was used. A convergence of 10⁻⁶ eV/atom was placed as a criterion on the self-consistent convergence of the total energy. The ions involved are steadily relaxed toward equilibrium until the Hellman–Feynman forces are minimized to less than 0.02 eV/Å using conjugate gradient algorithm during all relaxation runs. A further local optimization was done on the already relaxed structure using quasi-Newton algorithm until the Hellman–Feynman forces on the ions were less than 0.005 eV/Å. To represent electronic-correlation effects for a particular ionic configuration, the calculations used the generalized gradient approximation of Perdew and Wang (GGA-PW91). For cluster calculations, a cubic supercell of side of 20 Å was used and the Brillouin zone was sampled at the Γ point. For all the AlH₃ condensed phases, Brillouin zone integrations were performed using 4×4×4 k-points as per the Monkhorst–Pack grid scheme. The reference configurations for valence electrons used were Al(3s²3p⁴) and H(1s²).

To parametrize REAXFF energy expressions, a fitting was done to a training set containing the DFT derived equations of state (EoSs) of pure Al and AlH₃ condensed phases, reaction energies, and bond dissociation profiles on small finite clusters. The bond and atom parameters for REAXFF energy functions (Tables I and II) were determined from Al–Al and Al–H bonds in small Al₃H₇ clusters such as AlH₃, Al₂H₆, Al₃H₉, Al₄H₁₂, Al₅H₁₅, Al₆H₁₈, Al₇H₂₁, and Al₈H₂₄ and from the EoSs and cohesive energies of Al-metal and AlH₃ condensed phases. The symbols of the parameters in Tables I–IV are shown in Refs. 13 and 16.

Table III shows the EEM parameters (EEM hardness η, EEM electronegativity χ, and EEM-shielding parameter γ). These parameters were optimized to fit Mulliken charge distributions of small representative structures (AlH₃, Al₂H₆, Al₃H₉, and Al₄H₁₂) obtained from DFT calculations. REAXFF successfully reproduces charge transfer for all the clusters considered. The partial charges fitted into the training set were obtained by performing a Mulliken charge distribution analysis in an all electron calculation in CRYSTAL. CRYSTAL implements a localized basis set approach. The radical factors in the all electron basis set are expressed as a linear combination of Gaussian-type functions of the electron-nucleus distance according to 85(s)11(sp)G and 5(s)11(sp)1(p)G contractions for Al and H, respectively.

<table>
<thead>
<tr>
<th>Atom</th>
<th>η (kcal/mol)</th>
<th>χ (kcal/mol)</th>
<th>γ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.9</td>
<td>1.8921</td>
<td>0.6191</td>
</tr>
<tr>
<td>H</td>
<td>6.5</td>
<td>4.1882</td>
<td>0.7358</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Bond</th>
<th>Dₑ⁻⁻⁻⁻⁻</th>
<th>Pₑ⁻⁻⁻⁻⁻</th>
<th>Pₑ⁻⁻⁻⁻⁻</th>
<th>Pₑ⁻⁻⁻⁻⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–H</td>
<td>93.4</td>
<td>−0.6599</td>
<td>8.7138</td>
<td>−0.08</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Atom</th>
<th>pₑ⁻⁻⁻⁻⁻</th>
<th>k₁₁</th>
<th>pₑ⁻⁻⁻⁻⁻</th>
<th>pₑ⁻⁻⁻⁻⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>−23.18</td>
<td>2.53</td>
<td>8.0</td>
<td>2.5791</td>
</tr>
<tr>
<td>H</td>
<td>−15.76</td>
<td>2.15</td>
<td>1.0</td>
<td>2.8793</td>
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</table>
TABLE IV. Valence angle parameters.

<table>
<thead>
<tr>
<th>Angle</th>
<th>$\Theta_0$</th>
<th>$k_\sigma$</th>
<th>$k_\rho$</th>
<th>$p_{\sigma,1}$</th>
<th>$p_{\sigma,2}$</th>
<th>$p_{\rho,1}$</th>
<th>$p_{\rho,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–Al–Al</td>
<td>66.95</td>
<td>39.1233</td>
<td>0.1935</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>2.99</td>
</tr>
<tr>
<td>H–Al–Al</td>
<td>180.00</td>
<td>−26.6261</td>
<td>5.3467</td>
<td>1</td>
<td>0</td>
<td>1.0</td>
<td>1.01</td>
</tr>
<tr>
<td>H–Al–H</td>
<td>70.85</td>
<td>3.4517</td>
<td>8.8151</td>
<td>0</td>
<td>3.0</td>
<td>0</td>
<td>2.40</td>
</tr>
<tr>
<td>Al–H–Al</td>
<td>0.00</td>
<td>36.0088</td>
<td>0.0603</td>
<td>0</td>
<td>3.0</td>
<td>0</td>
<td>1.01</td>
</tr>
</tbody>
</table>

*The value leads to an equilibrium angle of 180°−0°=180° for the single bond Al–H–Al valence angle.

To ensure high numerical accuracy the truncation tolerance for the numerical evaluation of bielectronic integrals (both the Coulomb and the Hartree–Fock exchange series) were set at $10^{-8}$, $10^{-10}$, $10^{-8}$, and $10^{-16}$. All the units are in a.u. (1 a.u. = 627.51 kcal/mol).

Table IV shows the optimized valence angle parameters for H–Al–Al and H–Al–H angles. To obtain these quantities, the clusters are first fully optimized in DFT calculations. This is followed by doing single point calculations in which the valence angles are modified while other parameters are fixed. The first line reflects a normal H–Al–Al angle interaction, with an equilibrium angle of 113.05° and force constants of 39.1233 and 0.1935 kcal/mol. The valence angle with a negative force constant (H–Al–Al), −26.6261 kcal/mol, aims to destabilize the case where the hydrogen atom is exactly in between the Al atoms (i.e., H–Al–Al angle is zero degrees). This is effectively an inverted angle function, with a maximum at H–Al–Al equals zero degrees and falling off to zero for different values of this angle.

**A. Bond dissociation, angle bending, and binding energies**

Figure 1(a) shows the bond dissociation curve of AlH$_3$, while Fig. 1(b) shows the angle bending-energy curve of the AlH$_3$ molecule used to optimize the valence angle parameter of REAXFF.$\_{\text{AlH}_3}$. These DFT curves were used to optimize the bond energy in the reactive potential. The dissociation curves were constructed from the equilibrium geometry using single point calculations by changing the bond length. REAXFF gives an equilibrium bond length of 1.6 Å, which is in excellent agreement with DFT value of 1.59 Å. The energies were computed with reference to the equilibrium bond length’s energy. To optimize the valence angle parameter the geometry of the AlH$_3$ molecule was minimized for various fixed values, viz $120^\circ$, $115^\circ$, $110^\circ$, ..., $65^\circ$, $60^\circ$. REAXFF predicts that the H–Al–H equilibrium angle is $120^\circ$. This is in excellent agreement with DFT. For smaller angles, DFT gives larger energy barriers than REAXFF due to electron–electron repulsion inherent in the former. For instance, at $60^\circ$ the AlH$_3$ is destabilized by 44.4 kcal/mol in DFT, whereas REAXFF, which does not care about electrons, gives a destabilization energy of 11.66 kcal/mol.

Table V shows the DFT values versus REAXFF values of adsorption energies of hydrogen on Al(111) surface. The adsorption energy $E_{\text{ads}}$ is defined as $E_{\text{ads}}=[E_{\text{sub}}−E_{\text{S}}−nE_{\text{H}}]/n$, where $E_{\text{sub}}$ is the total energy of hydrogen-adsorbed aluminum slab, $E_{\text{S}}$ is the total energy of aluminum slab, $E_{\text{H}}$ is the total energy of hydrogen atom (−25.79 kcal/mol), and $n$ stands for the number of adsorbed hydrogen atoms. In the context of this definition, $E_{\text{ads}}<0$ corresponds to exothermic adsorption. To calculate $E_{\text{ads}}$ two hydrogen atoms were placed 12 Å apart in a cubic box of side of 20 Å. The Brillouin zone was sampled at the gamma point. The total energy of the hydrogen atom was then taken as half the calculated total energy. The Al surface was modeled by a repeated slab of five layers, giving a slab thickness of 9.6 Å. A vacuum equivalent to a slab with five layers of aluminum atoms was imposed in the z-direction to separate the slab from its periodic images. H is adsorbed on one side of the slab only. The top two layers plus the H atom are relaxed while the bottom three layers are fixed at their bulk positions. The Brillouin zone was sampled using a well converged 9 × 9 × 1 $k$-points.

REAXFF gives decent adsorption energies in comparison to DFT predictions (Table V). From DFT calculations, atomic hydrogen preferably adsorbs on the fcc site. This is consistent with the work of Stumpf, who showed that H preferably adsorbs on the fcc site with an exothermic adsorption energy from −45.58 to −45.89 kcal/mol (depending on the coverage). This value can be slightly higher or lower depending on the exchange-correlation functional (LDA, PBE, or PW91) used. In agreement with Stumpf, we calculated the fcc adsorption energy to be −47.63 kcal/mol. From REAXFF, the adsorption energies for bridge, hcp, and top sites...
structures are preferred to singly bridged structures. In due to exchange-correlation effects, the doubly bridged Al$_5$H$_{15}$ clusters. These small clusters are shown in Fig. 2.

Cluster Al$_3$H$_9$ on terrace tandem with cluster fragmentation. Herein, we make a comparison between DFT's binding energies and REAXFF/REAXFF computations, it was seen that for Al$_n$H$_{3n}$ ($n \geq 4$) the doubly bridged structures are preferred while the singly bridged structures are unstable. This can be understood from the fact that the more the interconnectivity of the Al–H bonds the stronger the bonding. Doubly bridged structures have more bonds and therefore bound to be more stable than singly bridged structures. Table VII shows the binding energies of various (AlH$_3$)$_n$ clusters considered in this work. Here, the binding energy is defined as:

$$BE = -[E(Al_nH_{2m}) - E(Al_{fcc}) - mE(H_2)]/m,$$

(2)

where $E(P)$ is the total energy of particle P in the ground state. For molecular hydrogen, in DFT, $E_{tot} = -156.87$ kcal/mol. The total energy of molecular hydrogen was used because in REAXFF the total energy is computed with reference to the isolated atomic species. The DFT values are consistent with the works of Kawamura et al. However, Kawamura et al. used the total energy of atomic hydrogen instead of that of molecular hydrogen. Therefore, in Table VIII we make a comparison between DFT values and the work of Kawamura et al. using the total energy of atomic hydrogen, $E_{tot} = -25.79$ kcal/mol. There is an excellent match between our calculated DFT values and those from the work of Kawamura et al., which was done at the LCAO+GGA level of theory. It can be seen in the table that there is a slow decrease in binding energy per hydrogen of these clusters with increasing cluster size. This is contrary to the expectation that the binding energy per hydrogen should increase concomitantly with increase in cluster size. The decrease in the binding energy can be attributed to the fact that as the cluster size increases so does the free energy of pure aluminum clusters, which raises the cost of fragmenting the

![Image](image-url)

**Fig. 2.** Small representative [AlH$_3$]$_n$, $n=1–7$, clusters used in the training set of REAXFF.

are $-47.37$, $-44.80$, and $-45.87$ kcal/mol, respectively.

For Al(111) bcc site DFT gives a value of $-44.8$ kcal/mol per H, while REAXFF gives $-47.8$ kcal/mol. For Al(111) fcc site DFT predicts the adsorption energy to be $-47.63$ kcal/mol, while REAXFF gives $-49.24$ kcal/mol. For the Al(111) top site REAXFF predicts the adsorption energy to be $-47.14$ kcal/mol, which is in good agreement with the DFT value of $-45.87$ kcal/mol. The DFT calculated energy barrier for H hopping from the bridge to the fcc site is 2.07 kcal/mol. REAXFF gives a migration energy barrier of 2.7 kcal/mol, which is in excellent agreement with the DFT value. These values are in good agreement with those of Hjelmberg who determined the diffusion energy barrier of H molecules on Al$_{111}$ surface. The energies for various Al$_n$H$_{3n}$ clusters considered in this work. Here, the binding energy is defined as:

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<table>
<thead>
<tr>
<th>Site</th>
<th>DFT</th>
<th>REAXFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp</td>
<td>-44.80</td>
<td>-47.80</td>
</tr>
<tr>
<td>fcc</td>
<td>-47.63</td>
<td>-49.24</td>
</tr>
<tr>
<td>Top</td>
<td>-45.87</td>
<td>-47.14</td>
</tr>
<tr>
<td>Bridge</td>
<td>-47.37</td>
<td>-48.93</td>
</tr>
</tbody>
</table>

**Table VI.** Binding energies of AlH$_3$, Al$_2$H$_6$, and Al$_3$H$_9$ on Al(111) surface.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>DFT (kcal/mol)</th>
<th>REAXFF (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlH$_3$ on terrace (horizontal)</td>
<td>-20.98</td>
<td>-15.18</td>
</tr>
<tr>
<td>Al$_2$H$_6$ on terrace</td>
<td>-49.81</td>
<td>46.95</td>
</tr>
<tr>
<td>Al$_3$H$_9$ on terrace</td>
<td>-51.65</td>
<td>44.39</td>
</tr>
</tbody>
</table>

**Table VII.** Binding energies BEs (in kcal/mol H$_2$) of small AlH$_3$ clusters used in the training set.
aluminum clusters to accommodate hydrogen atoms.

In the condensed state, for each an every phase of AlH₃ (α, α', β, and γ) polymorphic modifications considered in this work, the DFT energies were computed for a broad range of volume describing both expansion and compression. Figure 3 shows the crystal structure of the four polymorphs of AlH₃ (α, α', β, γ) considered in this work. All the AlH₃ polymorphs are made up of three dimensional networks of AlH₆ units. α-AlH₃ crystallizes in the trigonal R³̂c space group, β-AlH₃ crystallizes in the cubic Fd̄₃m space group, α'-AlH₃ crystallizes in the Cmcm space group, and γ-AlH₃ crystallizes in the orthorhombic Pnnm space group.

The issue of the relative stability of AlH₃ polymorphic modifications is quite interesting. Experimentally, α-AlH₃ is the most stable polymorph for temperatures greater than or equal to 300 K. Theoretically, Ke et al., using DFT, found β-AlH₃ polymorphic modification of AlH₃ to be the structure with the lowest energy. It is possible that at 0 K the β-phase is indeed more stable than the α-phase as found by Ke et al. On the other hand, the relative energy differences between these two phase are in the order of 1 kcal/mol. It might be that it is difficult for DFT to resolve this small energy difference. We found that indeed the cubic β-AlH₃ has the lowest energy. However, this result seems to be an artifact of the pseudopotential (PP) used. For the PAW PPs the β-AlH₃ phase has the lowest energy, whereas for ultrasoft (US) PP α'-AlH₃ phase has the lowest energy, see Table IX. In both cases, however, the relative energy differences between α, α', and β phases are less than 1 kcal/mol. This implies that it should be possible for these phases to transform into one another at certain temperatures and pressures. In particular, since the β phase has more open channels, it can transform to the α phase during the desorption of molecular hydrogen but only if the α phase is more stable. We did not include the ZPE corrections. In the work of Ke et al., zero point energy (ZPE) corrections were included.

Figure 4 shows the EoS for the R³̂c (α-AlH₃), Fd̄₃m (β-AlH₃), Pnnm (γ-AlH₃), and Cmcm (α'-AlH₃) phases of AlH₃. ReaxFF correctly describes the EoS of the four phases of AlH₃ and excellently estimates their relative phase stability vis-à-vis the DFT’s predictions. For instance, DFT (PAW) predicts that β-AlH₃ is more stable than γ-AlH₃ by 0.76 kcal/mol H₂, whereas reaxFF gives a value of 0.02 kcal/mol H₂. The experimental heat of formation, for the condensed phase, of AlH₃ range from −2.37 ± 0.1 kcal/mol H₂ (Ref. 2) to −2.72 ± 0.2 kcal/mol H₂, while the calculated values are in the range from −1.66 kcal/mol H₂ (Ref. 36) to −2.95 kcal/mol H₂. For α-AlH₃ phase, both DFT and ReaxFF give bulk values that are consistent with the calculated values, with DFT giving a value of −2.36 kcal/mol H₂ and ReaxFF giving −3.01 kcal/mol H₂. These values were calculated by comparing to Al(fcc) at its most stable volume and 1.5 H₂ (gas).

During the thermal desorption process there might be phase transformations/crystal modifications or conforma-
tional changes in both Al and AlH₃ systems. Graetz et al.² showed that transitions between α, β, and γ phases are exothermic and likely to occur spontaneously even at room temperature. Further, Grove et al.³⁷ showed that in the case of deuterated Al, there is a phase transformation of both β-AlD₃ and γ-AlD₃ to α-AlD₃ starting at 353 and 363 K, respectively. Maehlen et al.³⁸ observed a phase transformation of γ-AlH₃ to α-AlH₃ during the decomposition process of the former. There have been claims that such transitions are expected and, in fact, are indicative that the system transforms to a less stable structure. However, it should be noted that the formation of the various polymorphs of AlH₃ depends on their preparation history. Second, a clear sign that the result-

III. DYNAMICS OF HYDROGEN DESORPTION

An important part of force field parametrization is to get the right reaction dynamics during the thermal decomposition of a cluster (or bulk) of aluminum hydride. Therefore, to ascertain that the force field reproduces the right thermal decomposition dynamics, we heated up a representative aluminum hydride cluster (Al₂H₆). Al₂H₆ decomposes endothermically as follows:

\[ Al₂H₆ \rightarrow Al₂H₄ + H₂, \quad \Delta H_r = 22.95 \text{ kcal/mol.} \] (3)

The transition state and the minimum energy path (MEP) for the process in Eq. (3) was calculated in VASP (DFT) using NEB.³⁹ This is shown in Fig. 5(i). In the NEB simulation it was ascertained that both end points were stable manifolds by performing frequency analysis. To get an accurate identification of the saddle point the climbing image flag was turned on.⁴⁰ This has the effect of driving up to the saddle point the image with the highest energy. This permits an accurate determination of the transition state. To compute the activation energy barrier, the image at the top of the MEP was further locally optimized in VASP using quasi-Newton algorithm. The barrier was calculated to be 51 kcal/mol. In REAXFF the barrier was calculated to be 50 kcal/mol. In general, the dissociation process is endothermic but since the transition state is at a higher energy than the end point, then a fall in potential energy during the stage where molecular hydrogen is released is expected, which indicates that this portion of the reaction is an exothermic process. This is also reflected in Fig. 5(ii), which shows the energy profile during a molecular dynamics (MD) simulation of a heating run of Al₂H₆ at 0.000 25 K/iteration. In the MD simulation, velocity Verlet algorithm was used and the temperature was increased linearly by velocity scaling. The dynamics of hydrogen desorption in the two instances are similar. In Fig. 5(ii) there is a slight rise in energy at about 600 ps. This energy rise occurs due to the distortion of the Al₂H₆ structure. Also shown in Fig. 5(ii), after fragmentation of Al₂H₆ into Al₂H₄ and H₂, are the various geometrical modifications of the resultant Al₂H₄ during the heating process. The most important point to note in Fig. 5(ii) is that like in DFT, the desorption of molecular hydrogen in MD simulation is accompanied by a fall in the potential energy just after the transition state. This gives confidence that the force field reproduces the right desorption dynamics in comparison to DFT.

Table X shows the approximate temperature at which molecular hydrogen was desorbed (cluster dissociation) from various AlₙHₙₙₙ clusters. These temperatures are an approximation. In reality, the true fragmentation/desorption temperatures might be much lower, subject to long equilibration times, which is beyond the timescale of our simulation. The
most important thing to note here is the decrease in fragmentation/desorption temperature with increase in the size of clusters.

In all the simulation runs, a heating rate of 0.000 25 K/iteration was used because at a heating rate of 0.0025 K/iteration molecular AlH3 (alane) remained intact throughout the heating range. There are a number of factors that contribute to the temperature at which molecular hydrogen is desorbed from the cluster. First, the length of equilibration. For instance, molecular hydrogen was only desorbed from Al5H15 after equilibrating at this temperature (1700 K) for 3500 ps (3.5 ns). When the cluster was heated up from 1 to 2000 K at a rate of 0.000 25 K/iteration, it fragmented into AlH3 and Al2H6 without molecular hydrogen being desorbed. Second, as mentioned in the foregoing, during the heating process these clusters fragment into smaller clusters (which reaggregate) prior to desorption of molecular hydrogen. This fragmentation and reagglomeration process occurs throughout the heating range, once the temperature of the cluster has been elevated (roughly at temperatures greater than 700 K, in the timescale of our simulation). We term this phenomenon as dynamic fragmentation-agglomeration. The reason for fragmentation is that at elevated temperatures the system is already at the threshold where it can fragment into smaller clusters. However, the fragments are less stable. As a result they again agglomerate so as to attain greater stability. The agglomeration process is exothermic and is therefore accompanied by a local rise in temperature. This local rise in temperature facilitates the dissociation of Al–H bonds resulting in the desorption of molecular hydrogen. The calculated activation energy for fragmentation of Al14H12 into smaller clusters is summarized in Table XI. During the heating process Al14H12 fragmented into smaller clusters as follows: First, it fragmented into Al13H9 + AlH3. This was then followed by reagglomeration and a further fragmentation into Al13H6, Al12H9, and H2.

As shown in Table XI, Al13H12 can fragment into Al13H6 and AlH3 at an energy cost of 21.16 kcal/mol (DFT). This is quite close to the dissociation reaction Al13H12 → Al12H10 + H2, which costs 20.92 kcal/mol. This shows that it is possible that during the heating up process a given cluster of (Al13H12) can fragment into smaller clusters prior to desorption of molecular hydrogen once the temperature required to facilitate fragmentation has been reached.

The DFT calculated activation barrier of AlH3 fragmentation (i.e., AlH3 → Al + H2) in the gas phase is 96.94 kcal/mol and that for Al2H6 decomposition (i.e., Al2H6 → AlH2 + H2) is 51 kcal/mol. By comparison the experimental activation energy for hydrogen desorption in α-AlH3 is 23.22 kcal/mol. The activation energy barrier for fragmentation of alane is almost four times that for desorption of molecular hydrogen from bulk AlH3. This large difference cannot be due to computational inaccuracies. This implies that the fragmentation temperature of alane is much higher than the temperature of desorption of hydrogen from bulk AlH3. For instance, in the timescale of our simulation, we find that molecular hydrogen dissociates from Al2H6 at about 1900 K. For bulk AlH3, in the timescale of our simulation, molecular hydrogen desorbs at 700 K. This is clearly much less than the dissociation temperature of alane. From this comparison, it is clear that alane dissociates at a relatively higher temperature in comparison to bigger clusters. It follows therefore that if alanes were to be the facilitators of mass transport of aluminum atoms during the thermal decomposition of NaAlH4 (as suggested in Refs. 20 and 21), there must be a different mechanism by which they can release molecular hydrogen at lower temperature. One mechanism is that alanes undergo oligomerization. We discuss this issue in Sec. III A.

### A. Gas phase behavior of alanes

Figure 6(a) shows the dimerization of two AlH3 molecules, while Fig. 6(b) shows the agglomeration of two Al2H6 molecules resulting in the formation of a doubly bridged Al14H12 molecule. The NVT (constant number of particles, constant volume, and constant temperature) simulation was done at 300 K using Berendsen thermostat for 30 ps. The molecules were placed in a cube of side of 20 Å. The dimerization of AlH3 molecules is in agreement with the well known fact that as the size of AlH3 clusters increases so does its stability with respect to the individual AlH3 species. Higher alanes can be easily formed from smaller alanes since the agglomerated alanes are more stable than the individual alane species. The theoretical formation energies of Al14H12 molecule from two alane molecules as computed by DFT and REAXFF are −19.47 kcal/mol AlH3 and −18.2 kcal/mol AlH3, respectively. The DFT value is consistent with the previous works in Refs. 43–46. From Fig. 6(a), the dimerization energy for alanes is approximately −19 kcal/mol per AlH3. This is consistent with the calculated value in Table XII, which shows the energy of agglomeration of various small clusters of Al13H12 series as calculated using DFT and

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### TABLE XI. The heat of fragmentation of Al14H12 into various clusters during thermal heating of the cluster. The DFT values were computed using vasp at the PW91 level of theory. The energies are in kcal/mol.

<table>
<thead>
<tr>
<th>Starting products</th>
<th>DFT(PW91)</th>
<th>REAXFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al14H12 → Al13H10 + H2</td>
<td>20.92</td>
<td>18.77</td>
</tr>
<tr>
<td>Al13H9 + AlH3</td>
<td>21.16</td>
<td>29.15</td>
</tr>
<tr>
<td>AlH3 + Al12H9 + H2</td>
<td>28.82</td>
<td>32.61</td>
</tr>
<tr>
<td>Al12H9 + 2AlH3 + H2</td>
<td>67.75</td>
<td>66.93</td>
</tr>
</tbody>
</table>
To study the correlation between agglomeration and desorption of molecular hydrogen, we did a MD simulation using 20 Al$_2$H$_6$ molecules. We used Al$_2$H$_6$ molecules because Al$_2$H$_6$ molecule is more stable relative to two alanes (AlH$_3$ molecules). The molecules were placed at least 10 Å apart in a cubic box of side of 80 Å. The system was first minimized to find the nearest metastable state. After minimization, the system’s temperature was ramped up to 1000 K. This was then followed by a NVT MD equilibration period, using Berendsen thermostat. The temperature of 1000 K was chosen because we wanted to observe the desorption of molecular hydrogen during the agglomeration process. As will be shown later, even in the temperature range of 300–800 K agglomeration still takes place but molecular hydrogen is not desorbed. In the equilibration process, at 0 ps, the following molecules/clusters exists in the system: Al$_8$H$_{24}$, two Al$_9$H$_{18}$, two Al$_{10}$H$_{12}$, and six Al$_2$H$_6$. This is so because during the minimization and temperature ramping up process some of the Al$_2$H$_6$ molecules agglomerated. As illustrated in Fig. 7, at the end of the simulation there are two molecular hydrogens desorbed from the agglomerated cluster.

A number of factors contribute to desorption of molecular hydrogen. First, the agglomeration process is exothermic. Although, globally, the temperature is kept constant by a thermostat, there is a local rise in temperature due to exothermic nature of the agglomeration process. This local rise in temperature facilitates the instantaneous dissociation of the Al–H bond. Therefore, it becomes easy to desorb molecular hydrogen at this temperature (1000 K). Second, the growth of the cluster leads to the existence of many surface atoms, which are weakly bonded to aluminum atoms. Bigger clusters provide more facile paths for hydrogen desorption as they can make Al–Al metal bonds to compensate for the loss of Al–H bonds. Although the local rise in temperature during the agglomeration process might play a role in hydrogen desorption, in the long term limit, large cluster size effect is the major contributor to desorption of molecular hydrogen.

In Fig. 7 the snapshot at 0 ps shows the initial clusters after being heated up to 1000 K. Already at this stage some Al$_2$H$_6$ molecules have agglomerated. Notice the ringlike conformation of Al$_{20}$H$_{120}$ in Fig. 7. At 260.9375 ps the cluster present in the system is Al$_{40}$H$_{120}$, implying that all the small clusters have agglomerated into one cluster. At 261 ps the cluster undergoes partial fragmentation leading to the formation of Al$_{39}$H$_{117}$ and AlH$_3$. This partial fragmentation and reagglomeration goes back and forth throughout the simulation period. The first molecular hydrogen is desorbed at 267.875 ps, leading to the formation of the following clusters/molecules: Al$_{39}$H$_{114}$, AlH$_4$, and H$_2$. Actually, the AlH$_4$ moiety is quite unstable and is immediately reabsorbed back by the bigger cluster. At 286.25 ps we have the following clusters/molecules: Al$_{40}$H$_{116}$, Al$_{39}$H$_{115}$, and H$_2$. At the end of the simulation (1000 ps) the clusters/molecules present in the system are Al$_{40}$H$_{116}$ and two molecular hydrogen. What is quite interesting is that in the end structure (at 1000 ps) there is a central aluminum atom which has six neighboring hydrogen atoms. This is illustrated in Fig. 7(b). The central aluminum atom is in a pentagonal ring of aluminum atoms, which resembles the coordination of aluminum in β-AlH$_3$.

In a different simulation run, in which the temperature of the system was kept fixed at 800 K, the Al$_2$H$_6$ molecules agglomerated into Al$_{40}$H$_{120}$ cluster during the 500 ps simulation run. However, at this temperature no molecular hydrogen was desorbed. Further tests (simulations) showed that in the temperature range of 300–800 K the Al$_2$H$_6$ clusters agglomerated into one cluster (Al$_{40}$H$_{120}$). However, in these cases no molecular hydrogen was desorbed from the cluster. Figure 8(a) shows the agglomerated structure while the pair distribution function for the annealed (to 0 K) agglomerated cluster is illustrated in Fig. 8(b). The figure shows that the radial distribution function has a slightly broad delta peaks. This suggests that the cluster is in a quasicrystalline state. The quasicrystalline state can be explained by the fact that the aluminum and hydrogen atoms are somehow arranged in a semiperiodic pattern. The average Al–Al distance is approximately 3.0 Å. This value compares quite well to the DFT calculated Al–Al bond length in β-AlH$_3$ (3.2 Å). However, this structure does not have the local coordination of any of the condensed phases of AlH$_3$. There are some central

### Table XII. The energy of agglomeration (per AlH$_3$) of various small clusters of the Al$_2$H$_6$ series as calculated using DFT and REAXFF.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>DFT</th>
<th>REAXFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2AlH$_3$ → Al$_2$H$_6$</td>
<td>−19.47</td>
<td>−18.17</td>
</tr>
<tr>
<td>3AlH$_3$ → Al$_3$H$_9$</td>
<td>−20.86</td>
<td>−22.46</td>
</tr>
<tr>
<td>4AlH$_3$ → Al$<em>4$H$</em>{12}$</td>
<td>−20.94</td>
<td>−23.88</td>
</tr>
<tr>
<td>5AlH$_3$ → Al$<em>5$H$</em>{15}$</td>
<td>−22.19</td>
<td>−24.74</td>
</tr>
<tr>
<td>6AlH$_3$ → Al$<em>6$H$</em>{18}$</td>
<td>−20.90</td>
<td>−25.27</td>
</tr>
</tbody>
</table>
Al atoms that are five coordinated in hydrogen, while the rest have four hydrogen neighbors. The changes in charge redistribution as a result of agglomeration (i.e., plots of the clusters at the beginning of the simulation and that of the agglomerated cluster at the end of the simulation run) are shown in Fig. 9. The figure shows that at the end of the simulation run (500 ps), there is an upward shift on the charge on aluminum atoms as compared to at the beginning of the simulation. Therefore there is a substantial charge transfer from aluminum atoms to hydrogen atoms during the agglomeration process. The distribution of charge on aluminum atoms is also less than the nominal charge of aluminum, implying that the bonding between Al and hydrogen is covalent. Although there is an increase in the negative charge on hydrogen atoms a considerable number still have charges in the range $-0.1$ to $-0.5$. These are the surface hydrogen atoms as can be seen in Fig. 8.

IV. ABSTRACTION OF MOLECULAR HYDROGEN

An important question in hydrogen storage is knowing the nature of structural transformation that takes place during the desorption process of hydrogen. In order to get a better insight of structural transformation during the desorption of hydrogen, we simulated successive abstraction of surface molecular hydrogen from a representative aluminum hydride nanoparticle (Al$_{28}$H$_{84}$ cluster). This is illustrated in Fig. 10. The abstraction process of surface molecular hydrogen is given by:

$$\text{Al}_{28}\text{H}_n \rightarrow \text{Al}_{28}\text{H}_{n-2} + \text{H}_2,$$

where $n = 84 - 0$. The desorption energy is defined as

$$E_{\text{desorb}} = [E_{\text{Al}_{28}\text{H}_{84-n}} + E_{\text{n/2H}_2}] - E_{\text{Al}_{28}\text{H}_{84}},$$

where $n = 2, 4, 6, 8, \ldots, 48, 50, 52, \ldots, 84$.

Systematically, in the abstraction process, clusters were first minimized and then annealed to 0 K using MD simulation to find the nearest metastable conformation. After minimization, the temperature was ramped up to between 600 and 900 K at a rate of 0.025 K/iteration. This was then followed by a NVT (constant number of particles, constant volume, and constant temperature) equilibration period of 300 000 steps at this temperature (600–900 K) using Berendsen thermostat. In all cases, a time step of 0.25 fs was used. After the equilibration run, the clusters were annealed to 0 K at a rate of 0.0025 K/iteration. After this, molecular hydrogen was abstracted by removing two hydrogen atoms from the configuration at 0 K. This was done iteratively until all the hydrogen atoms were abstracted. The entire process was repeated several times, each time starting out with Al$_{28}$H$_{84}$ but with a different geometrical arrangement.
Only the energies of the most stable conformations that gave rise to the nearly smooth curve shown in Fig. 10 were considered.

Figure 10 shows the trend in particle stability as a function of hydrogen unloading. The negative values of the heat of formation show that at the initial stages the forward decomposition reaction in Eq. (4) is thermodynamically favored. During the abstraction process, the exothermicity of the desorption process decreases with increasing abstraction of molecular hydrogen. When almost a half of the hydrogen atoms have been abstracted, the process becomes endothermic.

The observation can be understood as follows. Region (I) shows the high rate segment when desorption of molecular hydrogen is very favorable, while region (II) is the slow rate segment when desorption of molecular hydrogen systematically becomes unfavorable. The cluster size dependence of the desorption process is related to the local coordination of aluminum atoms with hydrogen. Therefore, the higher the concentration of hydrogen the more favored the decomposition of AlH3. Large aluminum clusters can be understood to have a bulklike decomposition as follows:

$$(\text{AlH}_3)_2 \rightarrow (\text{AlH})(\text{AlH}_3) + \text{H}_2. \quad (6)$$

The reaction in Eq. (6) should be interpreted as follows. The AlH3 unit from which the hydrogen is abstracted is embedded in other AlH3 units. There is a saturation of AlH3 species in the cluster such that each AlH3 species is surrounded by other AlH3 species. This provides facile paths for hydrogen desorption as they can make Al–Al metal bonds to compensate for the loss of H–Al bonds. The critical point in Fig. 10 is the point at which there is a transition from exothermicity to endothermicity. In other words, the abstraction of hydrogen starts to become unfavorable since the system is stabilized. We can understand the stable region as follows. There are fewer hydrogen atoms in comparison to aluminum atoms. This implies that the AlH3 units are dispersed within the system and not embedded in other AlH3 units. Therefore, the abstraction process essentially behaves like dissociation of AlH3, AlH3→AlH+H2, which is energetically unfavorable.

Intuitively, one is bound to think that as more and more surface hydrogen atoms are abstracted, the remaining hydrogen atoms should become subsurface and be strongly bound to the aluminum atoms (see Ref. 17). However, this is not the case. As more and more surface hydrogen atoms are abstracted the bulk hydrogen atoms come to the surface. In fact, for Al28H4, the bulk aluminum atoms are octahedrally coordinated to hydrogen atoms (the average bond lengths are $d_{\text{Al–H}} = 1.64$ Å and $d_{\text{Al–Al}} = 3.342$ Å), while for Al28H42 the bulk aluminum atoms are tetrahedrally coordinated to hydrogen atoms (average bond lengths are $d_{\text{Al–H}} = 1.65$ Å and $d_{\text{Al–Al}} = 2.843$ Å). In the case of Al28H4 the bulk aluminum atoms have no nearest hydrogen neighbors, instead they are icosahedrally coordinated to neighboring aluminum atoms. The average Al–Al bond length in this case is 2.75 Å. Notice that $d_{\text{Al–H}}$ remains almost constant throughout the abstraction process, whereas $d_{\text{Al–Al}}$ decreases toward the aluminum bulk value. The decrease in $d_{\text{Al–Al}}$ with increasing abstraction of molecular hydrogen implies that there is a transition toward metallization. On the other hand, the almost constant value of $d_{\text{Al–H}}$ shows that the Al–H bond length is independent of the chemical environment for a given system (in this case binary aluminum hydride). The observations detailed herein show that aluminum atoms prefer to form bond with each other rather than with hydrogen. Hydrogen atoms prefer to stay on the surface rather than subsurface sites and since the surface hydrogen atoms prefer to mostly occupy the less stable twofold (bridge) sites, it becomes easy to desorb them. On the Al(111) surface hydrogen prefers to occupy the three-coordinated hollow (fcc and hcp) sites. The fact that hydrogen atoms prefer to occupy the bridge sites in clusters of this size shows that the surface has a corrugated morphology. The behavior of aluminum hydride cluster is therefore very different from that of NaH.47 It is also markedly different from that of MgH2. Wagemans47 showed that the hydrogen atoms in hydrogen depleted magnesium hydride prefer to cluster together instead of being evenly distributed. Using REAXFF, Cheung et al.18 showed that there are no surface hydrogen atoms for hydrogen depleted Mg2xHx (x=2,4,6) systems.

![FIG. 10. Desorption energy $E^\text{desorb}$ as a function of number of H2 molecules abstracted from the system. The reference energy, shown by the dotted line, is the energy for Al32H64.](image-url)
We find a different behavior for hydrogen atoms in aluminum hydride systems. In a hydrogen depleted aluminum hydride cluster, the hydrogen atoms are randomly scattered over the aluminum rich surface. This can be seen in Fig. 11, which shows the geometries of the annealed clusters of Al_{28}H_{84}, Al_{28}H_{72}, Al_{28}H_{42}, and Al_{28}H_{4}. In the hydrogen deficient Al_{28}H_{4} cluster the hydrogen atoms prefer to occupy surface sites rather than bulk.

The dynamics taking place within the structure during the systematic abstraction of molecular hydrogen can be understood better by examining charge transfer. To investigate the changes in charge transfer due depletion of hydrogen atom, charge distribution plots were made for Al_{28}H_{84}, Al_{28}H_{42}, and Al_{28}H_{4} clusters during the abstraction runs. This is illustrated in Fig. 12. As shown in Fig. 12, in Al_{28}H_{84} there is a broad distribution of charges on both aluminum and hydrogen. This is because there are many subsurface and surface hydrogen atoms. The low charges are associated with surface atoms, which have less number of neighbors. As one moves from Al_{28}H_{84} to Al_{28}H_{4} the distribution of charges of aluminum atoms tends toward the lower numbers, and concomitantly there is an increase in the negative charge on hydrogen atoms. This is reflected in the charge distribution on Al_{28}H_{42} as illustrated in Fig. 12. However, we see in Fig. 12 that the charges located at the hydrogen atoms in Al_{28}H_{4} actually decrease. We can understand this disparity as follows. Since charge distribution is a function of the number of nearest neighbors, this shows that with increasing abstraction of hydrogen there is a decrease in the number of nearest neighbors of opposite charge for both aluminum and hydrogen. The four hydrogen atoms are not subsurface but rather occupy surface sites where they are lowly coordinated to aluminum neighbors. Therefore, they have less number of aluminum atom neighbors. This makes them to have low negative charges. In the case of aluminum, at this point the aluminum atoms have formed metallic bonds since the number of hydrogen in the system is negligible. In other words the system tends toward metallization. In Al_{28}H_{4} there are three aluminum atoms that have icosahedral coordination. These aluminum atoms, therefore, have a bulk coordination. This suggests that once almost half the hydrogen atoms have been removed the hydrogen deficient aluminum hydride tends toward metallization.

V. MOLECULAR HYDROGEN TRAPPED IN ALUMINUM HYDRIDE SOLID

For many years now, there have been discussions on the possibility of molecular hydrogen being trapped in the channels of potential hydrogen storage materials such as NaAlH_{4} and AlH_{3}.^{48–51} The issue of hydrogen molecules being trapped in cages or channels of hydrogen storage media will present the next technological challenges with a view to fully harnessing the storage capabilities of these systems. Trapped molecular hydrogen implies that not all the desorbed hydrogen diffuses out during the thermal decomposition process of the potential hydrogen storage materials. This reduces the efficiency of these materials. How to channel out these trapped hydrogen molecules from the system during the desorption process is clearly a nontrivial task. Using nuclear magnetic resonance (NMR) spectra, Herberg et al. deduced that there were molecular hydrogen trapped in small cages in the interstitial sites of NaAlH_{4}.^{52} Recent experimental work, using proton NMR, by Senadheera et al. showed that molecular hydrogen can be trapped in solid matrix of AlH_{3} during the thermal decomposition of AlH_{3}.^{53} To simulate this possibility a cluster of AlH_{3}, consisting of 472 atoms, was heated up. The cluster was built up from a supercell of \beta-AlH_{3} by removing the periodic boundary conditions. \beta-AlH_{3} has very open channels compared to the \alpha-phase.
atoms should re-emphasize that our cluster consisted of only 472
triax and for that matter other hydrogen storage materials. We
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previous REAXFF descriptions. We find that REAXFFAlH3
during its thermal decomposition.
hundreds of thousands of atoms. This implies that several
from 150 to 200 nm. Such a particle can contain as much as
ments, usually after ball milling, the size of the particles vary
urers, and EoSs for Al and AlH3 condensed phases, a reactive
files, charge distribution, reaction energy data for small clus-
VI. CONCLUSION
3.1 kcal/mol H2, which compares excellently with DFT
value of −2.36 kcal/mol H2. The experimental heat of for-
formation ranges from −2.37 ± 0.1 kcal/mol H2 (Ref. 2) to
−2.72 ± 0.2 kcal/mol H2.8
In the gas phase, there is a thermodynamically driven
agglomeration of AlH3 molecules due to the tendency of the
system toward attaining a lower free energy configurations.
In the initial stages the dominant factor contributing to des-
orption of hydrogen is the local rise in temperature during the
agglomeration process, which weakens/dissociates the
Al–H bond. However, as the size of the agglomerated cluster
increases the large cluster size effect starts to play a decisive
role in desorption of hydrogen. The other contributing factor,
to a smaller extent, is the intercluster attraction, which weak-
ens the Al–H bond leading to desorption of molecular hydro-
gen in a nearby cluster as the clusters move toward each
other. The presence of defects such as stepped surfaces ac-
celerates the formation of alane oligomers. These simulation
results, especially the oligomerization process, are qualita-
tively consistent with the experimental work of Go et al.54
who noted that heating of alanes at 360 K led to “loss of both
mobile and smaller alanes to higher alanes and to desorp-
ton.” They showed that small alane clusters do agglomerate
to form large clusters but added that experimental limitations
might hinder the observation of the resultant compound alu-
muninum hydride clusters.

In the abstraction process of molecular hydrogen, it was
seen that with increasing abstraction the remaining hydrogen
atoms prefer to occupy surface sites rather than subsurface
sites. This behavior is quite different from that of NaH (Ref.
17) and MgH2 (Refs. 18 and 47) clusters in which with in-
creasing abstraction of molecular hydrogen the remaining
hydrogen atoms prefer subsurface sites. In the gas phase,
there is a thermodynamically driven agglomeration of alane
molecules. In the process of agglomeration, molecular hy-
drogen is desorbed from the oligomer. Using the method of
MD, based on REAXFF, we have unambiguously identified a
molecular hydrogen trapped in the AlH3 matrix.

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FIG. 13. The arrow shows a hydrogen molecule trapped in AlH3 channel.

The resultant cluster was first minimized then equilibrated at
300 K. The equilibrated cluster was then heated to 800 K, at
a heating rate of 0.0025 K/iteration. This temperature (800
K) was maintained for 120 ps. Figure 13 shows a hydrogen
molecule, indicated by an arrow, trapped in the channels of
the cluster.

There are dispersive van der Waals interactions between
the trapped molecule and the walls of the cages. The trapped
molecular hydrogen easily diffuses along the channels into
different cages of the cluster. It was noticed that after some-
time the molecule escaped. At a faster heating rate the mo-
lecular hydrogen escaped at a much earlier time due to the
collapse of some cages of the cluster. Even at a constant
temperature of 500 K, the molecular hydrogen escaped after
sometime although at this temperature it took much longer
time to escape.

These results therefore presents an unambiguous identi-
fication that molecular hydrogen can be trapped in AlH3 ma-
trix and for that matter other hydrogen storage materials. We
should re-emphasize that our cluster consisted of only 472
atoms (with an approximate width of 1.6 nm). In experi-
ments, usually after ball milling, the size of the particles vary
from 150 to 200 nm. Such a particle can contain as much as
hundreds of thousands of atoms. This implies that several
hundreds or even thousands of molecular hydrogen can be
trapped in cages or interstitial sites within such a solid matrix
during its thermal decomposition.