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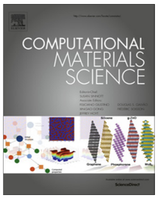

Study on electronic properties of α-, β- and γ-AlH_3 – The theoretical approach

M. Savić [*], J. Radaković, K. Batalović

Institute of Nuclear Sciences Vinča, P.O. Box 522, University of Belgrade, 11000 Belgrade, Serbia

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ABSTRACT

AlH_3 polymorphs (α-, β-, γ-) are highly promising materials for hydrogen storage and hydride electronics applications. Given the recent developments in the synthesis and hydrogen desorption approaches, here presented detailed comparison study of three AlH_3 polymorphs (α-, β-, γ-) is aimed to explain and potentially guide the improvements in applicability of these materials. We use electronic structure calculations based on the density functional theory (DFT) to address stability and bonding in α-, β- and γ-AlH_3. For better understanding of stability of various polymorphs, formation enthalpy of α′-AlH_3 is also addressed. Electronic properties (electronic density distribution, density of states, band structure and Bader's charge) are calculated using both generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) for exchange-correlation, as well as additional Tran-Blaha modified Becke-Johnson functional (TBmBJ) for exchange. Study shows interesting correlation of electronic structure and bond strength, not observed in previously reported studies of alanes, and presents results obtained using TBmBJ method applied on β- and γ-alanes. Band gaps, calculated using TBmBJ, are increased up to 96% as compared to the GGA-PBE values. Due to the lack of experimental data, strong conclusion on the applicability of TBmBJ for alanes cannot be made, although good agreement to G_0W_0 value and overestimation of GW value is seen in case of α-AlH_3. Band structure calculations lead to conclusions on electron mobility and other types of application beside hydrogen storage, while based on Bader's theory we compare bonding in all investigated polymorphs.

1. Introduction

Hydrogen has been studied as an attractive energy carrier for many years. The major disadvantage for the broad use of hydrogen energy is its storage, and storing hydrogen in suitable materials have shown to be an interesting option. Materials used for this purpose must be safe, recyclable, cheap, and have the ability to release hydrogen, which depends on their stability. This is the greatest focus of experimental research nowadays and the major problem to be overcome. Gravimetric target for on board hydrogen storage materials set by U.S. DOE (Department of Energy) went from 6 wt% hydrogen in 2010 to 9 wt% hydrogen in 2015 [1].

One promising material, which meets these preconditions, is AlH_3 (alane) with volumetric density of 0.148 kg H_2/l [2] and high hydrogen content of 10.1 wt% [3]. So far scientists have confirmed the existence of seven alane polymorphs α-, α′-, β-, γ-, δ-, ε-, ζ-. According to many studies, all AlH_3 polymorphs are metastable at ambient conditions, however using different synthesizing techniques it is possible to obtain the polymorph of interest. First synthesis of AlH_3 ether solvated form [4] and AlH_3 adduct ($C_6H_{12}N_2{\cdot}AlH_3$) [5] were reported over half century ago. Since then, organo-metallic synthesis of six AlH_3 polymorphs was reported [3]. Studies [6,7] report in detail organo-metallic synthesis of α-, β- and γ-AlH_3. Recently, mechanochemical synthesis showed many advantages over the chemical synthesis: it is greener (solvent free) and cheaper than the standard methods [8], giving the possibility to avoid environmental problems and to accelerate and simplify synthesizing process. Several AlH_3 polymorphs (α-, α′-, β-, and γ-) were synthesized during cryomilling of $LiAlH_4$ and $AlCl_3$ at low temperature [9]. Mechanochemical synthesis of α-AlH_3 [10] and α- and α′-AlD_3 [11], and γ-AlH_3 [12,13] under ambient conditions is reported. Synthesis of β-polymorph using mechanochemical method at ambient conditions is not noticed reviewing the literature.

Besides applications in hydrogen economy alanes are also very interesting due to their electronic structure, and could potentially find application in electronic devices, i.e. hydride electronics [14]. Karazhanov et al. [14,15] reported interesting properties of some AlH_3 phases, and classified alanes as wide band gap

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[*] Corresponding author.
E-mail address: msavic@vinca.bg.ac.rs (M. Savić).

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semiconductors, translucent to electromagnetic waves in VIS/UV range, having well dispersive bottommost CB (conduction band) and/or topmost VB (valence band) therefore allowing electronic conductivity. Recently, activation of α-AlH_3 using UV irradiation was demonstrated [16], showing how optical properties can be exploited to improve hydrogen storage properties.

In this work, we use theoretical approach to investigate crystal structure, stability and electronic features of α-, β- and γ-AlH_3, three most commonly synthesized alane polymorphs. The choice to investigate electronic properties is due to the fact that information regarding optical properties of β- and γ-AlH_3 is obtained so far using LDA and GGA exchange-correlation potentials, leading to well-known deficiency of DFT approach for semiconductors. Therefore, we hope to address systematically electronic properties of the studied polymorphs in order to explain and potentially enhance their performances for various applications, including hydrogen storage and electronic devices.

2. Computational details and methodology

Electronic structure calculations are performed based on DFT [17] using FP LAPW + lo (full potential linearized augmented plane waves + local orbital) method (implemented in wien2k [18] program package). For comparison, identical parameters for investigated polymorphs are used for $R_{MT}K_{max}$ (i.e. the size and the completeness of sets of basis function), and number of k-points (i.e. the quality of Brillouin zone sampling). Parameters are set as follows: R_{MT} (Al) = 1.75 bohr, R_{MT} (H) = 0.95 bohr, $R_{MT}K_{max}$ is set to 9.20 for aluminum and 5.00 for polymorphs, while the magnitude of the largest vector G in the Fourier expansion is set to 20 $bohr^{-1}$. The k-points sampling is performed using $14 \times 14 \times 14$ grid for Al, α- and β-polymorphs, and $11 \times 8 \times 10$ grid is used for γ-polymorph. Energy to separate core and valence states is -6.0 Ry, treating $3s^2$ $3p^1$ Al states and $1s^1$ H states as valence. As a charge convergence criterion, the charge difference between two iterations in self-consistent field cycles is chosen 0.00005e. The relaxation of crystal structures, according to the lattice symmetry, is performed by minimizing the forces that affect atoms until they became less than 1 m Ry $bohr^{-1}$. Exchange-correlation (XC) interactions are treated within general gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [19] during the structure optimization. In order to accurately address band structure, and given that energy of CB minimum is dependent on the exchange and correlation terms of the potential, additional calculations are done after structure optimization. Modified version of the Becke-Johnson potential is used (TBmBJ – uses local density approximation and modified Becke-Johnson density functional (LDA-mBJ)) for exchange [20], that adds a small amount of nonlocal Hartree-Fock (HF) exchange to the semi local density functional. Bader's [21] quantum theory of atoms in molecules (AIM) is used to investigate the character of bonds.

3. Results and discussion

3.1. AlH_3 polymorphs - crystal structures and stability

Fig. 1 shows crystal structures of Al and AlH_3 polymorphs. α- and β-AlH_3 have hexagonal and cubic unit cell respectively, while γ-AlH_3 has orthorhombic unit cell with two nonequivalent Al atoms and four nonequivalent H atoms. Fig. 1(d) and (e) show two hydrogen atoms, labeled as H-2 and four atoms labeled as H-4 that surround Al-1 atom, and atoms H-1, H-2, two H-3 and two H-4 surround Al-2 atom.

Comparing to Al which crystallizes in the fcc structure (space group Fm-3 m, calculated lattice parameter a = 4.0395 Å (4.0460 [22])), Al atoms in investigated polymorphs form a distorted face-centered structure (tilted in different angle for each polymorph). 6 H atoms octahedrally coordinate each Al atom. Calculated lattice parameters and atomic positions of AlH_3 polymorphs are given in Table 1, while Table 2 gives interatomic distances of H-H, Al-H, and Al-Al.

In addition to α-, β-, and γ-AlH_3, in Table 1 we also report relaxed structure of α'-polymorph; it was calculated in order to complement investigation of thermodynamics of the studied alanes. Optimized structural parameters for all phases are in good agreement with experimental and previously reported theoretical results, with discrepancies less than 2%, which is in range of GGA-DFT precision. Possible reasons for small deviations are using different theoretical approach (e.g. high-pressure study [27]) experimental conditions [28]. The volume of formula unit is the greatest for β-AlH_3 while α-AlH_3 has the smallest unit cell volume. Large volume related to β-AlH_3 formula unit is due to the large distance between neighboring octahedra (3.9 Å, Fig. 1c). This could imply structural changes under different conditions (high pressure, temperature), as also noticed by Vajeeston et al. [31].

Calculated Al-H distances (Table 2) within all structures vary in range from 1.70 Å to 1.76 Å. It is noticed that Al-H distances in β-AlH_3 octhahedra are 1.725 Å (exp. value of 1.712 Å [28]), which is close to interatomic distances between Al and H in α-AlH_3 octahedra, 1.717 Å (experimental value 1.715 Å [25]). Interatomic distance between two H atoms in β-AlH_3 is the shortest among investigated polymorphs, in accordance with report of Brinks et al. [28]. Crystal structure and calculated interatomic distances are in agreement with previously reported results [24–26,31].

AlH_3 polymorphs are metastable and do not decompose at ambient conditions due to the existence of Al_2O_3 layer [32]. However, at elevated temperatures they decompose according to the reaction (1) exhibiting low decomposition enthalpy.

$$AlH_3 \rightarrow Al + 3/2H_2 \tag{1}$$

Reaction (1) is not easily reversible due to the entropy term [33], pointing out that Al does not absorb hydrogen under moderate temperature and pressure, and that high hydrogen gas pressure is needed (P > 2.5 GPa) [34]. However, enthalpy term is important because it reflects the stability of the Al-H bond. AlH_3 shows low enthalpy of formation as compared to other non-reversible hydrogen storage materials. For α-AlH_3, experiments show that decomposition is a single step process [35], while for β-AlH_3 [36] it is reported that during decomposition phase transition to α'-AlH_3, is followed by transformation to more stable α–AlH_3 occurs before decomposition to Al and H_2. Also, γ-AlH_3 transforms to α-AlH_3 during decomposition [35]. For β- to α- transition, measured enthalpies are -1.0 kJ/mol H_2 [37] and -2.99 kJ/mol [31], while for γ- to α-measured values are -1.9 kJ/mol H_2 [38] and -1.14 kJ/mol [31]. For α'- to α-AlH_3 transition, reported energy difference is -1.1 kJ/mol H_2 [36] and -0.4 kJ/mol [31]. However, some experiments show that β-AlH_3 can decompose directly if suitable conditions are applied (i.e. lower temperature [6] or faster heating [36]); similar holds for γ-polymorph [39].

Pressure also lead to phase transitions among various alane polymorphs. γ-AlH_3 transforms into the α-AlH_3 in the pressure range 1–2 GPa, at medium temperatures [40]. Study of Drozd et al. [41] reported that β-AlH_3 is stable below 6 GPa, while with further pressure increase, it transforms to α-AlH_3.

To compare stability of three polymorphs we calculated enthalpy of formation, reaction (2). Enthalpy change in reaction (1) can be approximated by the change in electronic energy calculated from first principles [42,43] between product and reactants of the reaction. Energy of hydrogen molecule is obtained in [44] using the same exchange correlation (XC) functional.