Electronic structures and thermodynamic stabilities of aluminum-based deuterides from first principles calculations*

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The alanates (complex aluminohydrides) have relatively high gravimetric hydrogen densities and are among the most promising solid-state hydrogen-storage materials. In this work, the electronic structures and the formation enthalpies of seven typical aluminum-based deuterides have been calculated by the plane-wave pseudopotential method, these being AlD_3, $LiAlD_4$, Li_3AlD_6, $BaAlD_5$, Ba_2AlD_7, $LiMg(AlD_4)_3$ and $LiMgAlD_6$. The results show that all these compounds are large band gap insulators at 0 K with estimated band gaps from 2.31 eV in AlD_3 to 4.96 eV in $LiMg(AlD_4)_3$. The band gaps are reduced when the coordination of Al varies from 4 to 6. Two peaks present in the valence bands are the common characteristics of aluminum-based deuterides containing AlD_4 subunits while three peaks are the common characteristics of those containing AlD_6 subunits. The electronic structures of these compounds are determined mainly by aluminum deuteride complexes (AlD_4 or AlD_6) and their mutual interactions. The predicted formation enthalpies are presented for the studied aluminum-based deuterides.

Keywords: hydrogen storage material, complex aluminohydrides, electronic structures, density functional theory

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1. Introduction

The large scale utilisation of hydrogen as a fuel crucially depends on the development of compact hydrogen storage materials with a high mass content of hydrogen. One of the most attractive groups of materials is light weight aluminum based hydrides (namely alanates) because of their high gravimetric capacities.[1,2] Examples of promising alanates with high hydrogen contents are $LiAlH_4$ (10.6 wt%), $NaAlH_4$ (7.5 wt%), Li_3AlH_6 (11.1 wt%), $Mg(AlH_4)_2$ (9.3 wt%), $Ca(AlH_4)_2$ (7.9 wt%) and $LiMg(AlH_4)_3$ (9.7 wt%).[2] However, for these hydrides, there are still some problems in the reversibility of hydrogenation and dehydrogenation reactions, and also in high decomposition temperatures and low reaction rates.

Alanates are usually referred to as complex hydrides because of the presence of anionic metal complexes (AlH_4 or AlH_6). Different anionic metal complexes and cation matrixes can form different alanates.[3−5] This provides a method to control the phase stability of alanates for practical use of hydrogen or tritium storage. Theoretical and experimental studies, however, have proved that some alanates such as Li_2NaAlH_6,[3] $LiAl_2H_7$ and $LiAl_3H_{10}$ do not exist virtually.[6] And all the reported alanates with different structures contain AlH_4 tetrahedra or AlH_6 octahedra[7−11] subunits in their cells. As for developing novel hydrogen storage materials, it is important to clarify the electronic structures and bonding behaviours of alanates with different crystal structures.[12−14]

Though many first principles calculations of alanates have been reported,[14−19] up to now, the differences and similarities in electronic structures of alanates with different crystal structures are still not well clarified. In addition, $BaAlD_5$, Ba_2AlD_7, $LiMg(AlD_4)_3$ and $LiMgAlD_6$ have typical crystal structures,[10,11,20] however, to the best of our knowledge, except $BaAlD_5$, their electronic structures have not yet been reported.

In the present study, using the density functional theory, we investigate the electronic properties of seven typical aluminum -based deuterides: AlD_3, $LiAlD_4$, Li_3AlD_6, $BaAlD_5$, Ba_2AlD_7, $LiMg(AlD_4)_3$ and $LiMgAlD_6$. The phase stabilities and interesting binding characteristics in these aluminum-based deuterides are presented. And according to these data,

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we discuss the differences and similarities in electronic structures of aluminum-based deuterides with different crystal structures.

2. Model and method

2.1. Calculation details

Structure determination of hydrides is confronted with a complexity that hydrogen is by far the lightest element. Though neutron diffraction (ND) is a poor tool to locate hydrogen in crystal lattices, it is very powerful if deuterated compounds are used. Recently, the crystal structures of many aluminum-based deuterides were experimentally reported. For comparison with the experimental values, all our calculations are on the basis of aluminum-based deuterides.

All the electronic structure calculations in this work are performed within the framework of density functional theory (DFT), using the PW91 generalised gradient approximation (GGA) functional.[21] A plane-wave ultrasoft pseudo-potential method as implemented in the CASTEP code[22] is employed. The geometric optimisation of a computational cell is carried out with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimisation algorithm[23] provided in this code. The main advantage of the BFGS is that cell optimizations in the mixed space of both internal and cell degrees of freedom can be performed. The Pulay density mixing scheme[24] is used to generate a new starting charge density during the self-consistent-field (SCF) total energy calculations. The SCF calculations are converged when the energy threshold is lower than 10^{-6} eV/atom. In order to reduce the error resulting from the choice of the plane-wave basis sets and k points, as well as to guarantee comparable computational precision, the cut-off energy is set to be 600 eV in all calculations. Moreover, a k-point spacing smaller than 0.03 Å^{-1} (1 Å=0.1 nm) is individually adjusted in reciprocal space. Total energy changes are finally reduced down to less than 1.0×10^{-5} eV/atom, and Hellman–Feynman forces acting on atoms are converged to less than 0.03 eV/Å. The present type of theoretical approach has been successfully applied to a large variety of hydrides to reproduce ambient- and high-pressure phases.[13,25,26]

2.2. Crystalline structure optimisation

It is known that AlD_3 exists in various forms of polymorphs. Among them α-AlD_3 is found to be the most stable.[27] α-AlD_3 has a rhombohedral structure with space group $R\bar{3}c$. The unit cell contains two formula units. The optimised lattice parameters are $a = 4.47$ Å and $c = 11.84$ Å, with the D atoms at $x = 0.628$. These values are in good agreement with the experimental values $a = 4.44$ Å, $c = 11.80$ Å, and $x = 0.628$.[9] In α-AlD_3, the aluminum atoms formed a distorted face centered structure, where each Al atom is octahedrally coordinated by D atoms with an Al–D distance of 1.72 Å. Each AlD_6 octahedron shared its corners with neighbouring octahedral and each D atom on a corner formed a bridge between two Al atoms. The octahedra are tilted with respect to one another because these bridges are not linear, i.e., the Al–D–Al bond angle is 141° as shown in Fig. 1(a).

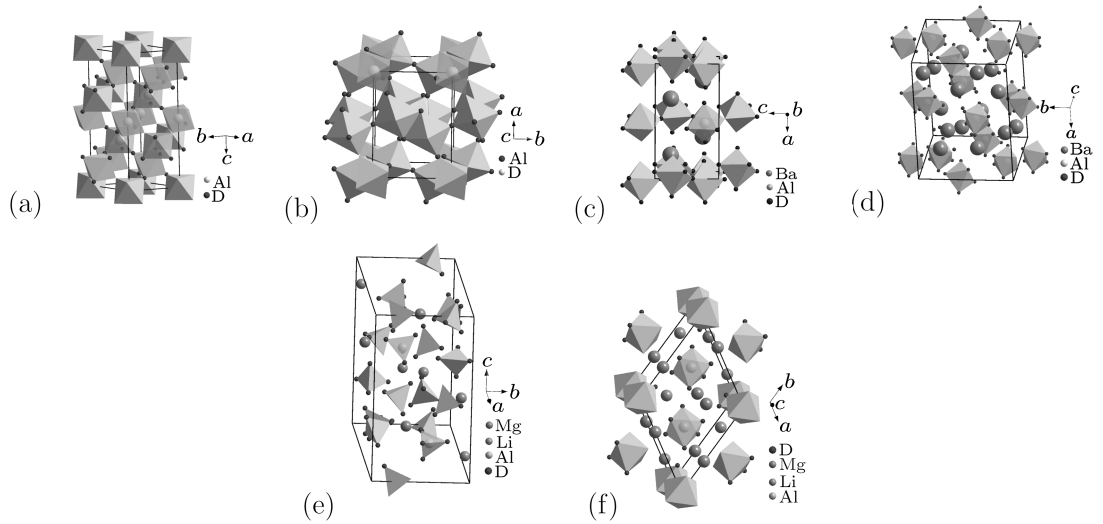


Fig. 1. Crystal structures of (a) α-AlD_3, (b) γ-AlD_3, (c) $BaAlD_5$, (d) Ba_2AlD_7, (e) $LiMg(AlD_4)_3$ and (f) $LiMgAlD_6$, where AlD_6 octahedra and AlD_4 tetrahedra are shaded.

Unique feature of double-bridge bonds involving Al–2D–Al is identified in γ-AlD_3.[17] Therefore, γ-AlD_3 contains the edge-sharing AlD_6 octahedral subunits. For comparison, the structure of γ-AlD_3 is also optimised.

The crystal structure of $BaAlD_5$ also contains corner-sharing AlD_6 octahedra, which form one-dimensional zigzag chains along the crystallographic c axis as shown in Fig. 1(c). These chains are surrounded by Ba atoms which form a distorted hexagonal network. Because of this interesting arrangement of the D atoms, $BaAlD_5$ has a larger D/M ratio than the most studied alanate $NaAlD_4$.[20] The calculated unit cell dimensions and positional parameters at 0 K and ambient pressures are in excellent agreement with the room temperature experimental findings for $BaAlD_5$.[20] The deviations in the unit-cell dimensions are almost zero (less than $\pm 0.5\%$) which are remarkably good for density functional calculations. Ba_2AlD_7 has a new structure type that could be built up from isolated AlD_6 units and infinite one-dimensional chains of edge-sharing DBa_4 tetrahedra.[31]

$LiMg(AlD_4)_3$ crystallises into the monoclinic $P2_1/c$ structure. This structure consists of a corner-sharing network of alternating isolated AlD_4 tetrahedra and LiD_6 or MgD_6 octahedra,[10] which is unlike that of $LiAlD_4$. The structure of $LiMgAlD_6$ consists of isolated AlD_6-octahedra linked together by Li and Mg atoms,[11] which is similar to that of Li_3AlD_6.

For comparison, we also carry out the optimisation calculations of $LiAlD_4$, $NaAlD_4$, $KAlD_4$ and Li_3AlD_6. The results are also listed in Table 1. The optimised lattice parameters are comparable to the experimental values within a deviation of less than 2.0%.

Table 1. Calculated and experimental structural parameters for studied deuterides.

compounds	space group	lattice parameters				Refs.
		a/Å	b/Å	c/Å	β(/°)	
α-AlD_3	$R\bar{3}c$	4.44	4.44	11.80		Exp.[9]
		4.47	4.47	11.84		This work
		4.49	4.49	11.80		Previous work [17]
γ-AlD_3	$Pnnm$	7.34	5.37	5.76		Exp.[28]
		7.32	5.34	5.71		This work
$LiAlD_4$	$P2_1/c$	4.83	7.80	7.90	112.27	Exp.[29]
		4.85	7.80	7.83	111.68	This work
Li_3AlD_6	$R-3$	8.07	8.07	9.51		Exp.[30]
		8.03	8.03	9.49		This work
$BaAlD_5$	$Pna2_1$	9.19	7.04	5.10		Exp.[20]
		9.19	7.07	5.10		This work
Ba_2AlD_7	$I2/a$	13.20	10.24	8.51	101.24	Exp.[31]
		13.15	10.29	8.53	101.18	This work
$LiMg(AlD_4)_3$	$P2_1/c$	8.37	8.74	14.30	124.83	Exp.[10]
		8.37	8.70	14.30	124.99	This work
$LiMgAlD_6$	$P321$	7.99	7.99	4.38		Exp.[11]
		7.93	7.93	4.35		This work
$NaAlD_4$	$I4_1/a$	4.98	4.98	11.15		Exp.[32]
		4.97	4.97	11.16		This work
$KAlD_4$	$Pnma$	8.74	5.73	7.26		Exp.[33]
		8.77	5.72	7.28		This work

3. Results and discussion

3.1. Electronic structures

The total density of states (DOS) of aluminum-based deuterides containing AlD_4 subunits are shown in Fig. 2(a). Electronic structure calculations are performed for $LiAlD_4$ with the full potential linear augmented

plane wave (FLAPW) method by Orgaz *et al.*[14] and Song and Guo.[34] The FLAPW method based on all electron calculations, however, is generally applicable only for relatively small unit cells. Up to now, only several aluminum-based hydrides such as $LiAlH_4$ and Li_3AlH_6[35] have been studied by this method. In the present work, we calculate the DOS of aluminum-based deuterides using the plane-wave pseudo-potential method. And we find that the DOSs of $LiAlD_4$ and Li_3AlD_6 are similar to the results calculated by the FLAPW method.[14,34]

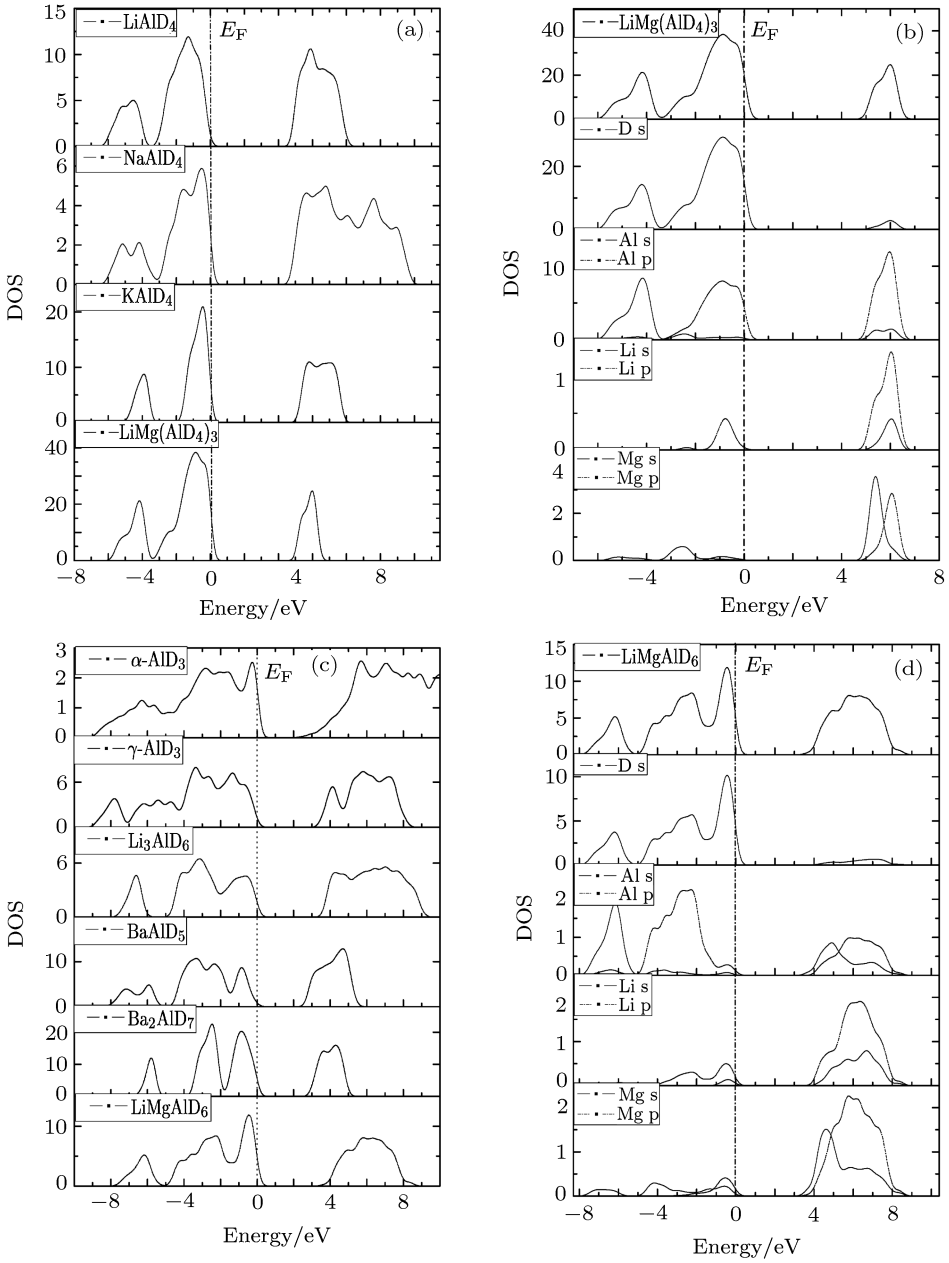


Fig. 2. Calculated electronic densities of states for (a) some aluminum-based deuterides containing AlD_4 subunits, (b) $LiMg(AlD_4)_3$, (c) some aluminum-based deuterides containing AlD_6 subunits and (d) $LiMgAlD_6$. The Fermi level is set to be zero and marked by a vertical line.

A larger band gap (~ 4.81 eV) could be seen between the valence band (VB) and the conduction band(CB) of $LiAlD_4$. And the valence DOS is separated into two regions as shown in Fig. 2(a). For comparison, the electronic structures of $NaAlD_4$, $KAlD_4$ and $LiMg(AlD_4)_3$ are also presented in Fig. 2(a). We note that there are two peaks in the valence DOS of these deuterides, though the crystal structures are different from each other.

The crystal structure of $LiMg(AlD_4)_3$ is newly published by Grove *et al.*[10] We have plotted the partial density of states (PDOS) of Li, Mg, Al and D atoms in Fig. 2(b). The bonding peaks in a lower region from −6.00 eV to −3.50 eV are due to the Al–D interactions between Al-3s and D-1s electrons within the AlD_4 subunits. The width of this region is ∼2.50 eV. The upper region from −3.20 to 0 eV is dominated by the D-1s and Al-3p electrons. The PDOS of Li and Mg are small in the VB.

The total DOS of aluminum-based deuterides containing AlD_6 subunits are shown in Fig. 2(c). The present results for the optimised structures of α-AlD_3, γ-AlD_3 and Li_3AlD_6 are comparable to previous calculations.[36] As for α-AlD_3, the valence DOS has a sharp peak just below the Fermi level and two more broad peaks at −2.5 eV and −6.0 eV below the Fermi level respectively. The lowest peak from −9.00 to −4.50 eV is found to correspond to D-1s and Al-3s states, while the higher energy features are composed of D-1s and Al-3p states[17] respectively. The total band widths are similar in both α- and γ-AlD_3. A difference between the two is clearly seen near −7.0 eV where a nearly separated DOS peak from −9.0 to −7.0 eV is present as shown in Fig. 2(b). This difference may be attributed to the different arrangements of AlD_6. For example, the AlD_6 octahedra in α-AlD_3 are corner-sharing, which strengthens the interaction between Al and D. On the whole, three peaks present in the valence DOS are the common characteristics of α- and γ-AlD_3, though they are overlapping in α-AlD_3.

Compared with the peaks of α-AlD_3 and γ-AlD_3, the three peaks are very obvious in the valence DOS of Li_3AlD_6, $BaAlD_5$, Ba_2AlD_7 and $LiMgAlD_6$. And it could be easily found that the valence band widths are shorten when the metal are cations combined with the subunits of AlD_6. The electrons are more localised in the valence DOS.

$BaAlD_5$ with a new orthorhombic structure in space group $Pna2_1$ is the first reported example that contains one-dimensional zigzag chains of AlD_6 along the crystallographic c axis.[20] The DOS of $BaAlD_5$, however, is still similar to those aluminum-based deuterides containing AlD_6. Ba_2AlD_7 contains many atoms in its cell. First principles calculations are time-consuming. To the best of our knowledge, the electronic structures of Ba_2AlD_7 and $LiMgAlD_6$ have not yet been reported before. Li_3AlD_6, Ba_2AlD_7 and $LiMgAlD_6$ have three distinct peaks in the valance DOS due to the crystal structures containing isolated AlD_6 subunits.

The PDOSs of aluminum-based deuterides containing AlD_6 subunits are very similar. Therefore, only the PDOS of $LiMgAlD_6$ is plotted and compared with that of $LiMg(AlD_4)_3$. The estimated band gap for $LiMgAlD_6$ is ∼ 3.96 eV, which is ∼ 1 eV smaller than that for $LiMg(AlD_4)_3$. The valence band of $LiMgAlD_6$ is extended about 2 eV lower in relative energy than that of $LiMg(AlD_4)_3$, by a split-off state originating from the interaction between the D-1s and Al-3p orbitals. And the VB is split into two separate region by a ∼0.5 eV energy gap. The first region from −8.0 to −5.3 eV originates mainly from the contributions of Al-1s states. The second region in the VB of $LiMgAlD_6$ is almost split by a pseudogap (at −1.4 eV) into a lower group of bands and an upper group, which is unlike that of $LiMg(AlD_4)_3$. The lower group of bands (from −4.8 to −1.5 eV) comprises energetically degenerated D-1s and Al-3p states which is favourable for the formation of a covalent bonding.[36] Therefore, there are three broad peaks in the VB of $LiMgAlD_6$. The hybridization of the Al orbital with the D orbital in $LiMgAlD_6$ is more localised within the valence band. And the contribution of D in the CB is small.

As a conclusion, we can obtain some important electronic properties of aluminum-based deuterides with different crystal structures. (1) All these compounds are insulators, and the band gaps are reduced when the coordination of Al varies from 4 to 6 (namely, from AlD_4 subunits to AlD_6 subunits). For example, the calculated band gaps are 2.31 eV in AlD_3, 4.81 eV in $LiAlD_4$, 3.67 eV in Li_3AlD_6, 4.96 eV in $LiMg(AlD_4)_3$ and 3.96 eV in $LiMgAlD_6$. Considering the fact that DFT underestimates band gaps, all these compounds are large band gap insulators.[18] And the change in coordination leads to the variation of the Al–D distance and consequently the shifts of the locations of VB and CB through variations in the orbital mixing.[19] (2) The electronic structures of the aluminum compounds are determined mainly by aluminum deuteride complexes and their mutual interactions. The VB comprises energetically degenerated D-1s and Al-3p states which are favourable for the formation of a covalent bonding. And in the VB, Al-3s and -3p states are separated. The contributions of Li, Ba or Mg in the corresponding VBs are small. And the VBs of these deuterides, to some extent, are dominated by the deuterium atoms, whereas the CBs

have mixed contributions from the deuterium atoms and the metal cations. (3) The VBs of aluminum-based deuterides containing AlD_6 are extended about 2 eV lower in relative energy than those containing AlD_4, by a split-off state originating from the interaction between the D-1s and Al-3p orbitals. (4) Two peaks present in the valence DOS are the common characteristics of aluminum-based deuterides containing AlD_4 subunits while three peaks are the common characteristics of aluminum-based deuterides containing AlD_6 subunits.

3.2. Thermodynamic stability

The electronic enthalpies of formation are determined by referencing the minimised compound ground state energy to the stoichiometric equivalent ground state energies of the constituent elements in their standard states. For example, the formation enthalpy of $LiAlD_4$ is calculated from the following equation:

$$\begin{aligned}&\Delta H(\mathrm{LiAlD_4}, 0\ \mathrm{K})\\ =\ &E_{\mathrm{tot}}(\mathrm{LiAlD_4}, 0\ \mathrm{K}) - E_{\mathrm{tot}}(\mathrm{Li}, 0\ \mathrm{K})\\ &- E_{\mathrm{tot}}(\mathrm{Al}, 0\ \mathrm{K}) - 2E_{\mathrm{tot}}(\mathrm{D_2}, 0\ \mathrm{K}),\end{aligned} \quad (1)$$

where ΔH ($LiAlD_4$, 0 K) is the formation enthalpy of $LiAlD_4$ evaluated at 0 K, and E_{tot} is the total energy of calculated cell. The total energy of D_2 is calculated by using the optimised bond length data with a cubic cell of $1 \times 1 \times 1$ nm^3 to avoid the interactions between the D_2 molecules.

From this equation, the formation enthalpy for $LiAlD_4$ is obtained to be -52.85 kJ·mol^{-1}·D_2^{-1} at 0 K without the consideration of the zero-point energy. Therefore, the prediction slightly underestimates its true value.[15] The present ground-state value, nevertheless, does not show much difference between a previously predicted value of -56.71 kJ·mol^{-1}·H_2^{-1} at 298 K[37] with consideration of the vibrational term, and the experimental value of -53.60 kJ·mol^{-1}·H_2^{-1} at 298 K. Hence, the vibrational term is not considered further in the present paper.

The predicted formation enthalpies for LiD, AlD_3 and Li_3AlD_6 are also in good agreement with the experimentally determined formation enthalpies. Table 2 also shows the enthalpies of reaction at 0 K for the decomposition reactions (4), (5) and (7). All these reactions are predicted to be endothermic. From the viewpoint of thermodynamic stability, the decomposition of $LiAlD_4$ would follow reaction (4) not reaction (5). And Li_3AlD_6 is more stable than $LiAlD_4$, which is in accordance with previous experimental findings.[38] Similarly, we can also conclude that $LiMgAlD_6$ is more stable than $LiMg(AlD_4)_3$.

Table 2. Calculated enthalpies for studied deuterides. For comparison, the obtained experimental values are given in parentheses.

compounds	reactions	No.	enthalpies (kJ·mol^{-1}·D_2^{-1})
LiD	$Li+1/2D_2 \rightarrow LiD$	(1)	–166.75(–167.8[39])
α-AlD_3	$Al+3/2D_2 \rightarrow AlD_3$	(2)	–12.08(–15.3,[38] –10.0[40])
$LiAlD_4$	$Li+Al+2D_2 \rightarrow LiAlD_4$	(3)	–52.85(–53.60[41])
	$LiAlD_4 \rightarrow 1/3\ Li_3AlD_6+2/3Al+D_2$	(4)	3.77(5.3,[41] 3.46[37])
	$LiAlD_4 \rightarrow LiD+Al+3/2D_2$	(5)	11.17
Li_3AlD_6	$3Li+Al+3D_2 \rightarrow Li_3AlD_6$	(6)	–98.17(–103.67[41])
	$1/3Li_3AlD_6 \rightarrow LiD+1/3Al+1/2D_2$	(7)	14.80(14.5,[37] 13.7[42])
$BaAlD_5$	$Ba+Al+5/2D_2 \rightarrow BaAlD_5$	(8)	–100.57
Ba_2AlD_7	$2Ba+Al+7/2D_2 \rightarrow Ba_2AlD_7$	(9)	–124.51
$LiMg(AlD_4)_3$	$Li+Mg+3Al+6D_2 \rightarrow LiMg(AlD_4)_3$	(10)	–35.28
$LiMgAlD_6$	$Li+Mg+Al+3D_2 \rightarrow LiMgAlD_6$	(11)	–65.19

The formation enthalpies for $BaA1D_5$ and Ba_2A1D_7 cannot be found in the scientific literature. The predicted values are –100.57 kJ·mol^{-1}·D_2^{-1} for $BaAlD_5$, and –124.51 kJ·mol^{-1}·D_2^{-1} for Ba_2AlD_7. The decomposition behaviour of $BaAlD_5$ is complicated. It has been reported that $BaAlD_5$ partly desorbed D_2 to form a mixture of $BaAlD_5$, Ba_2AlD_7, BaD_2, and $BaAl_4$ at 280 °C, whereas both $BaAlD_5$ and Ba_2AlD_7 are completely decomposed into BaD_2 and $BaAl_4$ at 350 °C.[41] From the calculated results, we can also conclude that Ba_2AlD_7 is more stable than $BaAlD_5$ as observed in experiment.[43]

4. Conclusions

The electronic structures and the formation enthalpies have been presented for the seven typical aluminum-based deuterides: AlD_3, $LiAlD_4$, Li_3AlD_6, $BaAlD_5$, Ba_2AlD_7, $LiMg(AlD_4)_3$ and $LiMgAlD_6$. The total band width is shortened when the metal cations are combined with the subunits of AlD_6 or AlD_4. And the VBs of aluminum-based deuterides containing AlD_6 are extended about 2 eV lower in relative energy than those containing AlD_4, by a split-off state originating from the interaction of the D-1s and Al-3p orbitals.

The electronic structures of these compounds are determined mainly by aluminum deuteride complexes and their mutual interactions. All these compounds are large band gap insulators at 0 K with the estimated band gaps from 2.31 eV in AlD_3 to 4.96 eV in $LiMg(AlD_4)_3$. The band gaps are reduced when the coordination of Al changes from 4 to 6. Two peaks present in the valence DOS are the common characteristics of aluminum-based deuterides containing AlD_4 subunits while three peaks are the common characteristics of those containing AlD_6 subunits. The calculated formation enthalpies revealed that $LiMgAlD_6$ is more stable than $LiMg(AlD_4)_3$ while Ba_2AlD_7 is more stable than $BaAlD_5$.

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