Ab initio study of magnesium alanate, Mg(AlH$_4$)$_2$

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(Dated: November 8, 2018)

Magnesium alanate Mg(AlH$_4$)$_2$ has recently raised interest as a potential material for hydrogen storage. We apply ab initio calculations to characterize structural, electronic and energetic properties of Mg(AlH$_4$)$_2$. Density functional theory calculations within the generalized gradient approximation (GGA) are used to optimize the geometry and obtain the electronic structure. The latter is also studied by quasi-particle calculations at the GW level. Mg(AlH$_4$)$_2$ is a large band gap insulator with a fundamental band gap of 6.5 eV. The hydrogen atoms are bonded in AlH$_4$ complexes, whose states dominate both the valence and the conduction bands. On the basis of total energies, the formation enthalpy of Mg(AlH$_4$)$_2$ with respect to bulk magnesium, bulk aluminum and hydrogen gas is 0.17 eV/H$_2$ (at $T = 0$). Including corrections due to the zero point vibrations of the hydrogen atoms this number decreases to 0.10 eV/H$_2$. The enthalpy of the dehydrogenation reaction Mg(AlH$_4$)$_2$ → MgH$_2$ + 2Al + 3H$_2$(g) is close to zero, which impedes the potential usefulness of magnesium alanate as a hydrogen storage material.

PACS numbers: 61.50.Lt, 61.66.Fn, 71.20.Nr

The interest in alanate compounds as hydrogen storage materials was recently rekindled as the kinetics of hydrogen adsorption/desorption improved dramatically by the addition of transition metal catalysts. Alanates MAIH$_4$, with M a lightweight alkaline earth metal, have a high gravimetric hydrogen density, which is essential for their application as storage materials. Most attention up to now has gone to sodium alanate, NaAlH$_4$, which has a hydrogen capacity of 7.5 wt. %\textsuperscript{2} It releases hydrogen in a two stage process. The two stages involve reaction enthalpies that are sufficiently small to be of interest, namely 0.38 and 0.34 eV per H$_2$ molecule respectively. However, only three out of four hydrogen atoms are released in this process, which lowers the effective hydrogen storage capacity. This has stimulated the search for other suitable alanates.

Alanates M(AlH$_4$)$_2$, with M a lightweight alkaline earth metal, have an even higher gravimetric hydrogen density. Recent interest turned to magnesium alanate, Mg(AlH$_4$)$_2$, which has a hydrogen capacity of 9.3 wt. %\textsuperscript{3,4}. Upon heating Mg(AlH$_4$)$_2$ releases hydrogen according to the reaction

\[
\text{Mg(AlH}_4\text{)}_2 \rightarrow \text{MgH}_2 + 2\text{Al} + 3\text{H}_2(g). \tag{1}
\]

Since decomposition of MgH$_2$ takes place at too high a temperature to be of practical use\textsuperscript{5,6,7,8} it is the amount of hydrogen released in \textsuperscript{1} that determines the actual storage capacity of Mg(AlH$_4$)$_2$. Still, this relatively large amount of 7.0 wt. % makes magnesium alanate a good candidate for hydrogen storage. Only little is known about the thermodynamics of this material, however.\textsuperscript{9,10} Since up to now its synthesis has proceeded via an indirect route, the first question is whether Mg(AlH$_4$)$_2$ is thermodynamically stable with respect to decomposition into its elements. The answer to this question is relevant in the search for a more direct synthesis route.

A second question concerns the reaction enthalpy of \textsuperscript{1}. The ideal hydrogen storage material should produce a hydrogen pressure of 0.1 MPa at room temperature. The entropy contribution of hydrogen gas at this temperature favors the right-hand side of \textsuperscript{1}. At $T = 0$ the hydrogen desorption reaction should therefore have an enthalpy of $\sim 0.4$ eV per desorbed H$_2$ molecule.\textsuperscript{2} Furthermore, the kinetics of hydrogen adsorption/desorption should be sufficiently fast. Finding ways of improving the kinetics can start from understanding the bonding in Mg(AlH$_4$)$_2$, which is determined by the electronic structure of the material.

In this paper we report the results of an ab initio study on the properties of magnesium alanate. The structure is optimized and the electronic structure is calculated. We characterize the bonding in Mg(AlH$_4$)$_2$ and calculate the enthalpy of formation from its elements, as well as the enthalpy of the dehydrogenation reaction \textsuperscript{1}.

Computational methods. Total energies are calculated within density functional theory (DFT), using the PW91 generalized gradient approximation (GGA) functional.\textsuperscript{12,13} We use the projector augmented wave (PAW) method\textsuperscript{12,13} and a plane wave basis set, as implemented in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{14,15,16}. The atomic positions and the cell parameters, including the cell volume, are optimized by minimizing the forces and stresses. A $7 \times 7 \times 7$ Monkhorst-Pack \textit{k}-point mesh is used for sampling the Brillouin zone.\textsuperscript{17} A kinetic energy cutoff of 312 eV is used for the plane wave basis set. The reaction enthalpies are calcu-
lated using a higher kinetic energy cutoff of 700 eV to ensure convergence.

If we calculate reaction enthalpies from total energy differences only, we neglect the contributions from atomic vibrations. Such contributions are negligible for heavy elements, whereas they may be significant for hydrogen. For each compound involved in the reaction we calculate its zero point vibrational energy (ZPVE), \( \frac{1}{2} \hbar \sum \omega_j \), resulting from the vibrational modes \( j \) in the optimized structure. Vibrational frequencies \( \omega_j \) are generated from a dynamical matrix, whose matrix elements (i.e., the force constants) are calculated using a finite difference method.\(^{25}\) For the hydrogen molecules we calculate a ZPVE of 0.29 eV, in good agreement with the value of 0.27 eV obtained from the experimental frequency.\(^{22}\) We also consider the zero point rotational energy (ZPRE) of the hydrogen molecules. Assuming that ortho- and para-hydrogen are produced in a proportion of three to one, the average ZPRE of a hydrogen molecule is 0.011 eV, using the energy levels given in Ref. 19. In summary, the reaction enthalpies \( \Delta H \) are calculated from

\[
\Delta H = \sum_f \left( E_{f,\text{tot}} + E_{f,\text{ZPVE}} \right) + E_{H_2,\text{ZPRE}} - \sum_i \left( E_{i,\text{tot}} + E_{i,\text{ZPVE}} \right)
\]

where \( E_{f,\text{tot}} \) denotes the total electronic energy of the reaction products \( f \) or reactants \( i \), \( E_{f,\text{ZPVE}} \) are the corresponding ZPVEs, and \( E_{H_2,\text{ZPRE}} \) is the ZPRE of all hydrogen molecules involved in the reaction.

DFT calculations using the common density functional\(^{23,26,24}\) give adequate values for ground state properties such as total energies and vibrational frequencies. Excited state properties are not given accurately, e.g., the electronic band gap is typically underestimated by \( \sim 50\% \). This in fact stems from an unjustified interpretation of the Kohn-Sham eigenvalues of DFT as excitation energies. To calculate single-particle excitation energies, one should solve a quasi-particle equation using the non-local, energy dependent self-energy. The GW technique approximates the self-energy by a dynamically screened exchange interaction. Constructing this interaction from the orbitals and eigenvalues obtained in a DFT calculation with the local density approximation (LDA) is called the \( G_0W_0 \) approximation. It leads to accurate band structures and band gaps for a wide range of semiconductors and insulators.\(^{22,26}\) GW calculations have also been successfully applied to metal hydrides.\(^{22,24}\)

We start from an LDA calculation using norm conserving pseudo potentials and a plane wave kinetic energy cutoff of 748 eV.\(^{22,24}\) The screened interaction \( G_0W_0 \) is then calculated using the real space, imaginary time formalism.\(^{22,24}\) For these calculations we use 150 LDA states, a \( 13 \times 13 \times 19 \) real space grid sampling of the unit cell, and an interaction cell consisting of \( 5 \times 5 \times 4 \) unit cells. The quasi-particle equation is solved while neglecting the off-diagonal elements of the self-energy between the LDA states. We estimate that the quasi-particle band gap of \( \text{Mg(AlH}_4)\text{$_2$} \) is numerically converged to within \( \pm 0.06 \) eV.

\[\text{FIG. 1: (Color online) Crystal structure of Mg(AlH}_4)_2; space group P3m1}\]

\[\text{TABLE I: Optimized crystal structure of Mg(AlH}_4)_2, compared to the experimental structure at 8 K from Ref. 8}\]

| Crystal structure. Magnesium alanate has a CdI$_2$ structure with the Mg atoms on the Cd positions and AlH$_4$ tetrahedra on the I positions; the space group is P3m1 (164).\(^{7,8}\) The structure basically consists of AlH$_4$ tetrahedra which form close packed double layers perpendicular to the c-axis, alternated with a layer of Mg atoms, as shown in Fig. 1. Starting from the experimental structure proposed in Ref. 8, we optimize the atomic positions and cell parameters. As it turns out, for unit cell volumes in the range 125-150 Å$^3$ the total energy only weakly depends upon the volume. We map out the total energy as a function of the cell volume. At each volume we optimize the atomic positions and the cell shape, and allow for breaking the symmetry. Interpolating this energy versus volume curve gives a minimum energy at a cell volume of 143.26 Å$^3$. Optimizing the structure at this volume gives the final results shown in Table I. The calculated structure has P3m1 symmetry and is in good agreement with the recently obtained experimental structure extracted from X-ray and neutron powder diffraction data.\(^{8}\) The Al-Al nearest neighbor distance within a double layer is 3.91 Å, whereas the shortest Al-Al distance between two double layers is 4.66 Å. Mg atoms occupy octahedral interstitial sites between two double layers with Mg-Al distances of 3.50 Å. The AlH$_4$ tetrahedra are slightly distorted, but they retain a threefold rota-
tion axis parallel to the c-axis. The Al-H1 and Al-H2 bond lengths are 1.60 and 1.62 Å, and the H1-Al-H2 and H2-Al-H2 bond angles are 113.0° and 105.8°. The geometry of the AlH4 tetrahedra is similar to that found in isolated (AlH4)− ions, where the Al and H atoms are covalently bonded. This geometry is quite different from those found in neutral AlH4 clusters. The minimum Al-H and H-H distances between atoms of different AlH4 tetrahedra is 3.14 Å and 2.63 Å respectively, indicating that the AlH4 tetrahedra are clearly separated. The Mg atoms are octahedrally coordinated by H2 atoms with a Mg-H distance of 1.89 Å and H-Mg-H angles of 86.9° and 93.1°. This coordination is not unlike that found in MgH2.

Electronic structure. Fig. 2(a) shows the electronic density of states (DOS) of magnesium alanate obtained from the DFT/GGA calculation. It can be compared to the calculated DOS of the lattice of (AlH4)− tetrahedra, shown in Fig. 2(b). Here the Mg ions have been removed and replaced by a homogeneous positive background charge. The similarities between Figs. 2(a) and (b) demonstrate that the (AlH4)− ions strongly contribute to both the valence and the conduction bands of Mg(AlH4)2. Such a dominance of the anion is also observed in the simple ionic compound NaCl.

Projecting the valence states on atomic orbitals shows that Al and H contribute a comparable amount, which is a strong indication for covalent bonding within the (AlH4)− tetrahedra. The splitting into two valence bands, as is most clearly visible in Fig. 2(b), is a remnant of the splitting between states of s-like (A1) and p-like (T2) symmetry in a single tetrahedron. In an isolated (AlH4)− ion, the sp-gap is ~ 4 eV. This gap is closed to a certain extent by the interaction between the (AlH4)− ions, which results in a band dispersion of 2-3 eV. It shows that, although the interaction between the (AlH4)− tetrahedra is not negligible, it is weaker than the interaction within a single tetrahedron.

If we compare the valence bands of Figs. 2(a) and (b) in more detail, we observe a small peak in the DOS of Mg(AlH4)2, which occurs within the sp-gap mentioned above. This peak results from the hybridization between H and Mg s states. Hybridization with Mg p and d states also gives less clearly visible contributions at higher energy. In any case, the H-Mg hybridization is much weaker than the H-Al hybridization.

The DFT/GGA band structure of Mg(AlH4)2 is shown in Fig. 3. It has an indirect band gap of 4.4 eV. The bottom of the conduction band is at A and the top of the valence band located at maximum of AH 0.7AH, [A = (0, 0, 0), H = (0, 0, 0, 0)]. The band gap as obtained from the G0W0 calculation is 6.5 eV. This classifies Mg(AlH4)2 as a large band gap insulator, which is typical for ionic compounds. The dispersions of the highest valence and the lowest conduction bands in a direction along the c-axis are rather small. The direct band gap at A is 6.9 eV; the direct band gap at Γ is 6.9 eV. More generally the dispersion of the G0W0 bands is very similar to that of the GGA bands. The total band width, 6.0 eV, of the G0W0 valence bands is ~ 0.1 eV larger than the GGA valence band width.

The layered structure of Mg(AlH4)2, see Fig. 1, does not imply that the interactions in the compound are strongly anisotropic. The dispersions of the bands in various directions are similar, compare e.g. the ΓA and the ΓM directions [M = (0, 0, 0)]

Formation enthalpy. The formation enthalpy of Mg(AlH4)2 with respect to its elements corresponds to the enthalpy of the reaction

\[
\text{Mg(AlH}_4\text{)}_2 \rightarrow \text{Mg} + 2\text{Al} + 4\text{H}_2(g).
\]  

Here Mg and Al are in the crystalline phase, whereas H2 is in the gaseous phase. For aluminum we use the fcc structure with a lattice parameter of 4.05 Å and for magnesium we used the hcp structure with lattice parameters \(a = 3.21\) Å, \(c = 5.21\) Å. The total energies and ZPE corrections are given in Table I. From these numbers, the reaction enthalpies are then calculated using Eq. (2).
TABLE II: Total energies (with respect to non spin polarized model atoms), zero point vibrational energies (ZPVE) and zero point rotational energy (ZPRE) in eV/formula unit.

|       | \( E_{\text{TOT}} \) | \( E_{\text{ZPVE}} \) | \( E_{\text{ZPRE}} \) |
|-------|----------------------|----------------------|----------------------|
| Mg    | −1.524               | 0.001                |                      |
| Al    | −3.698               | 0.004                |                      |
| H₂    | −6.792               | 0.294                | 0.011               |
| MgH₂  | −8.983               | 0.402                |                      |
| Mg(HAl₄)₂ | −36.764               | 1.520                |                      |

The reaction enthalpy of \( \text{MgH}_2 \) with respect to its elements

\[
\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2(g).
\]

The reaction enthalpy of \( \text{MgH}_2 \) is 0.67 eV/H₂ without ZPE corrections and 0.57 eV/H₂ with ZPE corrections. This value is in reasonable agreement with the value of 0.76 eV/H₂, which is extracted by extrapolating the experimental results to zero temperature.

The calculated reaction enthalpy of \( \text{MgH}_2 \) is 0.003 eV per H₂ molecule in the gas phase, without ZPE correction. This is negligibly small, but consistent with earlier experimental data. Moreover, including the ZPE correction makes the reaction enthalpy actually slightly negative, i.e. −0.06 eV/H₂. In any case this number is significantly less than the ∼0.4 eV/H₂ which, based on thermodynamics, is required to make Mg(HAl₄)₂ a good material for hydrogen storage. Further investigations are needed to see whether e.g. alloying would increase the stability of magnesium alanate.

Acknowledgments. We thank Prof. Dr. R. A. de Groot, Prof. Dr. P. J. Kelly, and Dr. B. Dam for helpful discussions. This work is part of the research programs of ‘Advanced Chemical Technologies for Sustainability (ACTS)’ and ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, financially supported by ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)’.

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