

***Ab initio* study of $\text{Mg}(\text{AlH}_4)_2$**

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Magnesium alanate $\text{Mg}(\text{AlH}_4)_2$ has recently raised interest as a potential material for hydrogen storage. We apply *ab initio* calculations to characterize structural, electronic and energetic properties of $\text{Mg}(\text{AlH}_4)_2$. 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. $\text{Mg}(\text{AlH}_4)_2$ 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 reaction enthalpy for decomposing $\text{Mg}(\text{AlH}_4)_2$ into 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 $\text{Mg}(\text{AlH}_4)_2 \rightarrow \text{MgH}_2 + 2\text{Al} + 3\text{H}_2(g)$ is close to zero, which impairs the potential usefulness of magnesium alanate as a hydrogen storage material.

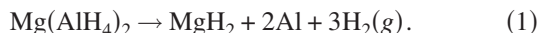
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I. INTRODUCTION

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.^{1,2} Alanates MAlH_4 , with M a lightweight alkaline 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. %.²⁻⁴ 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 $\text{M}(\text{AlH}_4)_2$, with M a lightweight alkaline earth metal, have an even higher gravimetric hydrogen density. Recent interest turned to magnesium alanate, $\text{Mg}(\text{AlH}_4)_2$, which has a hydrogen capacity of 9.3 wt. %.⁵⁻⁸ Upon heating $\text{Mg}(\text{AlH}_4)_2$ releases hydrogen according to the reaction



Since decomposition of MgH_2 takes place at too high a temperature to be of practical use,^{2,9} it is the amount of hydrogen released in (1) that determines the actual storage capacity of $\text{Mg}(\text{AlH}_4)_2$. 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.¹⁰ Up until now its synthesis has proceeded via an indirect route, so the first question is whether $\text{Mg}(\text{AlH}_4)_2$ 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 (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 (1). At $T=0$ the hydrogen desorption reaction should, therefore, have an enthalpy of ~ 0.4 eV per desorbed H_2 molecule.² Furthermore, the kinetics of hydrogen adsorption/desorption should be sufficiently fast. Finding ways of improving the kinetics can begin from understanding the bonding in $\text{Mg}(\text{AlH}_4)_2$, 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 $\text{Mg}(\text{AlH}_4)_2$ and calculate the enthalpy of decomposition into its elements, as well as the enthalpy of the dehydrogenation reaction (1).

II. COMPUTATIONAL METHODS

Total energies are calculated within density functional theory (DFT), using the PW91 generalized gradient approximation (GGA) functional.¹¹ We use the projector augmented wave (PAW) method^{12,13} and a plane wave basis set, as implemented in the Vienna *Ab initio* Simulation Package (VASP).¹⁴⁻¹⁶ 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 \mathbf{k} -point mesh is used for sampling the Brillouin zone.¹⁷ A kinetic energy cutoff of 312 eV is used for the plane wave basis set. The reaction enthalpies are calculated 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 vi-

brations. 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), $\frac{1}{2}\hbar\sum_j\omega_j$, resulting from the vibrational modes j in the optimized structure. Vibrational frequencies ω_j are generated from a dynamical matrix, whose matrix elements (i.e., the force constants) are calculated using a finite difference method.¹⁸ 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.¹⁹ 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 ΔH are calculated from

$$\Delta H = \sum_p (E_p^{\text{tot}} + E_p^{\text{ZPVE}}) + E_{H_2}^{\text{ZPRE}} - \sum_r (E_r^{\text{tot}} + E_r^{\text{ZPVE}}) \quad (2)$$

where $E_{p/r}^{\text{tot}}$ denotes the total electronic energy of the reaction products p or reactants r , $E_{p/r}^{\text{ZPVE}}$ are the corresponding ZPVEs, and $E_{H_2}^{\text{ZPRE}}$ is the ZPRE of all hydrogen molecules involved in the reaction. By varying the computational parameters, in particular the PAW potentials, we estimate that reaction enthalpies are converged on a scale of 0.05 eV.

DFT calculations using the common density functionals 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 nonlocal, 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.²⁰ GW calculations have also been successfully applied to metal hydrides.^{21,22}

We start from an LDA calculation using norm conserving pseudo potentials and a plane wave kinetic energy cutoff of 748 eV.²³ The screened interaction G_0W_0 is then calculated using the real space, imaginary time formalism.^{22,24} For these calculations we use 350 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 $\text{Mg}(\text{AlH}_4)_2$ is numerically converged to within ± 0.02 eV.

III. CRYSTAL STRUCTURE

Magnesium alanate has a CdI_2 structure with the Mg atoms on the Cd positions and AlH_4 tetrahedra on the I posi-

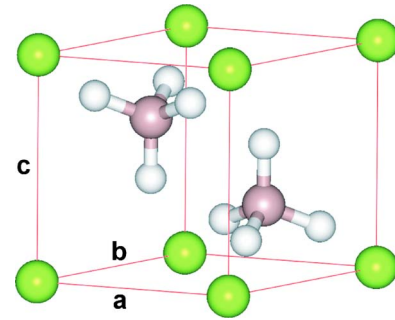


FIG. 1. (Color online) Crystal structure of $\text{Mg}(\text{AlH}_4)_2$; space group $\text{P}\bar{3}\text{m}1$.

tions; the space group is $\text{P}\bar{3}\text{m}1$ (164).⁷ 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. 7, we optimize the atomic positions and cell parameters. As it turns out, for unit cell volumes in the range $125\text{--}150 \text{ \AA}^3$ 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 \AA^3 . Optimizing the structure at this volume gives the final results shown in Table I. The calculated structure has $\text{P}\bar{3}\text{m}1$ 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 \AA , whereas the shortest Al—Al distance between two double layers is 4.66 \AA . Mg atoms occupy octahedral interstitial sites between two double layers with Mg—Al distances of 3.50 \AA . The AlH_4 tetrahedra are slightly distorted, but they retain a threefold rotation axis parallel to the c axis. The Al—H1 and Al—H2 bond lengths are 1.60 and 1.62 \AA and the H1—Al—H2 and H2—Al—H2 bond angles are 113.0° and 105.8° . The ge-

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

| Cell parameters | | a | b | c |
|-------------------|-------|-------|--------|-------|
| | calc. | 5.23 | 5.23 | 6.04 |
| | exp. | 5.21 | 5.21 | 5.84 |
| Wyckoff positions | | x | y | z |
| Mg (1a) | calc. | 0 | 0 | 0 |
| | exp. | 0 | 0 | 0 |
| Al (2d) | calc. | 1/3 | 2/3 | 0.706 |
| | exp. | 1/3 | 2/3 | 0.699 |
| H1 (2d) | calc. | 1/3 | 2/3 | 0.442 |
| | exp. | 1/3 | 2/3 | 0.424 |
| H2 (6i) | calc. | 0.168 | -0.168 | 0.812 |
| | exp. | 0.167 | -0.167 | 0.811 |

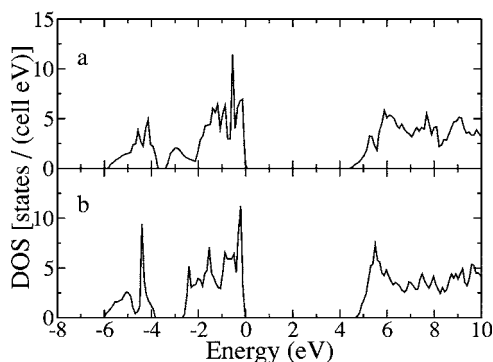


FIG. 2. (a) The DFT/GGA electronic density of states (DOS) of $\text{Mg}(\text{AlH}_4)_2$. The zero of energy is at the top of the valence band. (b) DOS of $(\text{AlH}_4)_2^-$ with a positive homogenous background charge.

ometry of the AlH_4 tetrahedra is similar to that found in isolated $(\text{AlH}_4)^-$ ions, where the Al and H atoms are covalently bonded.^{25,26} This geometry is quite different from those found in neutral AlH_x clusters.²⁷ The minimum Al—H and H—H distances between atoms of different AlH_4 tetrahedra is 3.14 and 2.63 Å, respectively, indicating that the AlH_4 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°.²⁵ This coordination is not unlike that found in MgH_2 .

IV. ELECTRONIC STRUCTURE

Figure 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 $(\text{AlH}_4)^-$ 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 2(b) demonstrate that the $(\text{AlH}_4)^-$ ions strongly contribute to both the valence and the conduction bands of $\text{Mg}(\text{AlH}_4)_2$. Such a dominance of the anion is also observed in the simple ionic compound NaCl.^{28,29}

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 $(\text{AlH}_4)^-$ 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 (A_1) and p -like (T_2) symmetry in a single tetrahedron. In an isolated $(\text{AlH}_4)^-$ ion, the sp -gap is ~ 4 eV. This gap is closed to a certain extent by the interaction between the $(\text{AlH}_4)^-$ ions, which results in a band dispersion of 2 to 3 eV. It shows that, although the interaction between the $(\text{AlH}_4)^-$ 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 2(b) in more detail, we observe a small peak in the DOS of $\text{Mg}(\text{AlH}_4)_2$, 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.

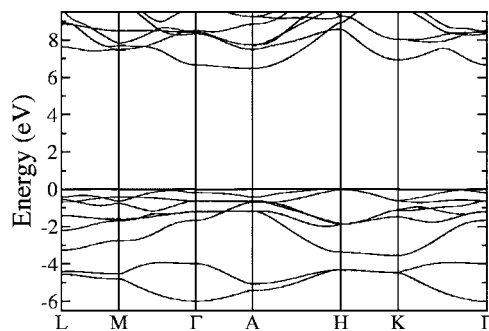


FIG. 3. GW band structure of $\text{Mg}(\text{AlH}_4)_2$. The zero of energy is at the top of the valence band.

The GW band structure of $\text{Mg}(\text{AlH}_4)_2$ is shown in Fig. 3. It has an indirect band gap, where the bottom of the conduction band is located at A and the top of the valence band at 0.7AH, [$A=(0,0,1/2)$, $H=(1/3,1/3,1/2)$]. The band gap as obtained from the G_0W_0 calculation is 6.47 eV. This classifies $\text{Mg}(\text{AlH}_4)_2$ 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 6.88 eV; the direct band gap at Γ is 6.85 eV. The total valence band width is 5.99 eV. The valence bands are split into two sets, the lower and upper set having a width of 2.05 and 3.57 eV, respectively. The two sets are separated by a small gap of 0.36 eV.

The layered structure of $\text{Mg}(\text{AlH}_4)_2$ 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 [$M=(1/2,0,0)$]. This indicates that the interactions between the ions within a layer (the ab plane) are comparable to those perpendicular to the layers.

V. REACTION ENTHALPIES

Decomposing $\text{Mg}(\text{AlH}_4)_2$ into its elements corresponds to the reaction



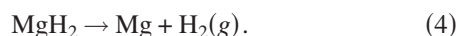
Here Mg and Al are in the crystalline phase, whereas H_2 is in the gaseous phase. For aluminum we use the fcc structure with a lattice parameter of 4.05 Å and for magnesium we used the hcp structure with lattice parameters $a=3.21$ Å, $c=5.21$ Å. The total energies and ZPE corrections are given in Table II. From these numbers, the reaction enthalpies are then calculated using Eq. (2).

The reaction enthalpy of (3) is 0.17 eV per H_2 molecule on the basis of total energies. If we include the ZPE, the reaction enthalpy decreases to 0.10 eV/ H_2 . Since the reaction enthalpy (3) is positive, it should, in principle, be possible to synthesize $\text{Mg}(\text{AlH}_4)_2$ from the elements. Note that at this energy scale, the contributions due to the zero point motions of the hydrogen atoms are not negligible. In general, they tend to make a negative contribution to the reaction enthalpy for decomposing the metal hydride, since the motion of a hydrogen atom in the crystal is more confined than in the gas phase.

TABLE II. Total energies (with respect to nonspin polarized model atoms), zero point vibrational energies (ZPVE) and zero point rotational energy (ZPRE) in eV/formula unit.

| | E^{TOT} | E^{ZPVE} | E^{ZPRE} |
|------------------------------------|------------------|-------------------|-------------------|
| Mg | -1.524 | 0.001 | |
| Al | -3.698 | 0.004 | |
| H ₂ | -6.792 | 0.294 | 0.011 |
| MgH ₂ | -8.983 | 0.402 | |
| Mg(AlH ₄) ₂ | -36.764 | 1.520 | |

To calculate the reaction enthalpy of (1) one also needs the optimized structure and ZPVE of MgH₂. MgH₂ has space group $P4_2/mnm$ (136) and its calculated lattice parameters are $a=4.51$ Å and $c=3.01$ Å. The magnesium and hydrogen atoms are at the $2a$ and $4f$ ($x=0.304$) Wyckoff positions, respectively. As a check on the accuracy of these calculations we can also extract the reaction enthalpy of decomposing MgH₂ into its elements



The reaction enthalpy of (4) is 0.67 eV/H₂ without ZPE corrections and 0.57 eV/H₂ with ZPE corrections. This is in reasonable agreement with the value of 0.76 eV/H₂, which is extracted by extrapolating the experimental results to zero temperature.^{9,30}

For other metal hydrides our calculations also underestimate the decomposition enthalpy, although usually by a smaller amount. This would indicate a systematic error of up to 0.2 eV on the calculated enthalpies, which is larger than the spread of 0.05 eV caused by using different PAW potentials.³¹ However, this does not alter our conclusions.

The calculated reaction enthalpy of (1) is 0.003 eV per H₂ molecule in the gas phase, without ZPE correction. This is negligibly small, but consistent with earlier experimental data.¹⁰ 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(AlH₄)₂ a good material for hydrogen storage. Further investigations are needed to see whether, e.g., alloying would increase the stability of magnesium alanate.

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