

First Crystal Structure Studies of CaAlH₅

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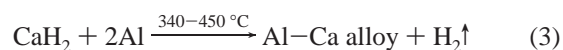
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A new member of the aluminum hydride family, CaAlH₅, is formed during the decomposition of Ca(AlH₄)₂. The crystal structure of this new compound was calculated by density functional theory band-structure calculations and confirmed by X-ray powder diffraction analysis. The structure crystallizes in space group *P*₂₁/*n* (No. 14), with *a* = 8.3797(9) Å, *b* = 6.9293(8) Å, *c* = 9.8138(11) Å, β = 93.78(1)°, and *Z* = 8.

Since Bogdanović and Schwickardi discovered that sodium alanate (NaAlH₄), doped with Ti as a catalyst, can be reversibly dehydrogenated and rehydrogenated,¹ complex aluminum hydrides became highly promising materials for H₂ storage applications. The limited storage capacity of 5.6 wt % H₂ of NaAlH₄ requires the extension of research to alternative complex hydride systems. Recently, it has been shown that, after dehydrogenation, Mg(AlH₄)₂ cannot be reversibly rehydrogenated.² The decomposition of LiAlH₄, which has a theoretical capacity of 10.6 wt % H₂, proceeds in a two-step process. The thermodynamically unstable LiAlH₄ does not allow applications for which reversibility is required. However, Chen et al.³ report a reaction enthalpy of 41.1 kJ/mol of H₂, which makes a reversible dehydrogenation of Li₃AlH₆ possible, but this result could not be confirmed by other groups. In principle, the hydrogen uptake and release is reversible for KAlH₄. Unfortunately, the process temperatures are quite high (250–330 °C),⁴ making this system less interesting for applications. The decomposition of Ca(AlH₄)₂ is a two-step process.^{2,5,6} During the

decomposition at about 100 °C, an intermediate phase appears, which was assigned to CaAlH₅.^{2,6} At higher temperatures, the decomposition of the intermediate phase results in the formation of CaH₂ and Al, and in a final step, Ca–Al alloys are formed [reactions (1)–(3)].



From experimental data, the decomposition for the first step [Ca(AlH₄)₂ to CaAlH₅] is found to be irreversible. Differential scanning calorimetry measurements indicate the possibility of a reversible rehydrogenation of the second step,² but so far this could not be confirmed by experimental data.

Recently, the crystal structure of Ca(AlH₄)₂ was predicted from density functional theory (DFT) band-structure calculations,⁷ but up to now, the structure of CaAlH₅ was unknown. The presence of multiple phases and the lack of any structural information in the former studies^{2,6} did not allow the unambiguous assignment of the observed peaks to CaAlH₅. It is known that the crystal structure could help in the understanding of the decomposition path and hydrogenation routes. Investigations of the mechanistic processes provide insights that are useful for the development of new systems. For this reason, CaAlH₅ with Al as a by-product was synthesized and analyzed by crystallographic methods. In this work, we report for the first time on the predicted crystal structure of CaAlH₅ and on the results of structure refinements.

DFT^{8,9} calculations were performed to investigate possible structures of the CaAlH₅ intermediate. The calculations were performed using the projector augmented wave (PAW) method^{10–12} with the PW91 exchange correlation functional,¹³

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Table 1. Calculated Energies (eV/Formula Unit) and Final Densities (kg/m³) for the CaAlH₅ Candidate Structures^a

space group	prototype	Z	ref	lattice	energy	density
<i>Pna</i> 2 ₁ (No. 33)	BaAlH ₅	4	18	orthorhombic	-24.63	1703
<i>P2</i> ₁ 2 ₁ 2 ₁ (No. 19)	α-BaAlF ₅	4	17	orthorhombic	-24.62	1713
<i>P2</i> ₁ / <i>n</i> (No. 14)	β-BaAlF ₅	8	17	monoclinic	-24.76	1765
<i>P2</i> ₁ (No. 4)	γ-BaAlF ₅	4	17	monoclinic	-24.65	1796
<i>P1</i> (No. 2)	δ-BaAlF ₅	6	16	triclinic	-24.72	1790
<i>C2/c</i> (No. 15)	CaAlF ₅	4	19	monoclinic	-24.48	1432
<i>Immm</i> (No. 71)	MgAlF ₅	2	20	orthorhombic	-24.40	1425
<i>P2</i> ₁ / <i>n</i> (No. 14)	α'-SrAlF ₅	8	16	monoclinic	-24.85	1693

^a The first five columns describe the candidate structure.

implemented in the program VASP.^{14,15} A plane-wave cutoff of 1000 eV was used. Ca 3s, 3p, and 4s electrons were included as valence electrons. A number of candidate structures were selected from known crystalline phases of MAIX₅ composition, mostly fluorides. CaAlH₅ structures based on each of the candidate structures were allowed to relax fully within the symmetry of the starting space group. In each case, a Γ -centered *k*-point grid of sufficient density was selected to converge the total energy to better than 1 meV per unit cell for the starting structure. Geometry optimizations (with simultaneous relaxation of atomic positions and lattice parameters) were considered converged when the total energy changed by less than 0.5 meV per unit cell for successive optimization steps.

As input models for the structure calculations, nine MAIX₅ candidate crystals were selected from the literature. Structures with more than eight formula units per unit cell were not considered because of computational constraints. A common feature of the selected structures is the presence of chains of corner-sharing AlX₆ octahedra. While in MgAlF₅ the chains are linear and perfectly aligned (with all bonded Al-F-Al angles being 180°) and CaAlF₅ possesses slightly distorted linear chains, the remaining structures possess zigzag chains in which each AlX₆ octahedron shares adjacent corners with two neighboring octahedra. The selected structures and the results of the geometry optimizations are summarized in Table 1. The energies are quoted relative to spherically symmetric reference atoms. The eight formula units per unit cell structure derived from the α'-SrAlF₅ structure of Weil et al.¹⁶ was found to be the most stable structure of those considered. This structure is isotypic with α'-BaFeF₅.¹⁷ The converged structure had a monoclinic unit cell with *a* = 8.3247 Å, *b* = 6.9665 Å, *c* = 9.7800 Å, and β = 94.22°.

The structure refinements were performed with the Rietveld program FULLPROF.^{21,22} The atomic coordinates

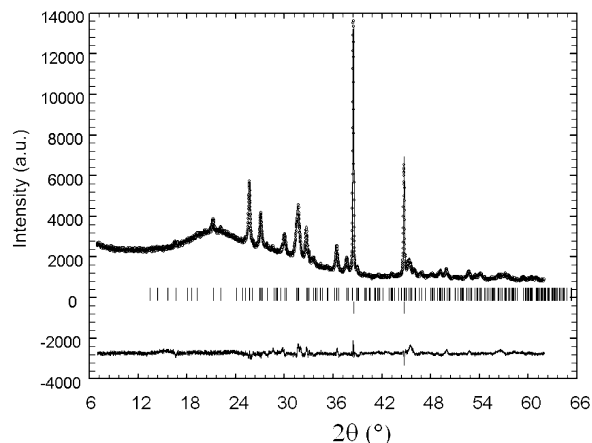


Figure 1. Final Rietveld plot of CaAlH₅. The marked reflection positions belong to CaAlH₅ (upper) and Al (lower).

obtained by the DFT calculations were used as the starting parameters (Table S2 in the Supporting Information). The measured patterns show a broadening of the profiles, indicating a small particle size and/or distortion of the structure. Also the presence of amorphous material complicates the structure analysis. The refinement of inorganic structures from X-ray powder data containing many H atoms is not trivial, and the refinement of the H positions themselves is impossible. Because of the weak X-ray scattering power of H, the positions of the H atoms cannot be determined with a high degree of accuracy. For this reason, we kept the H atoms fixed at the positions calculated by DFT methods, whereas the Al and Ca positions were refined. An independent refinement of the H positions requires neutron diffraction experiments of deuterium-exchanged samples. The powder patterns reported in previous studies^{2,6} showed CaAlH₅ to be present only as a minor component. Furthermore, no structural model for the compound was available. Here we present powder data of CaAlH₅ together with calculated crystal structure data. The results of the first refinement confirm the calculated structure model, isotypic with α'-SrAlF₅. However, additional structure investigations and neutron diffraction experiments are in preparation.

A comparison of the powder pattern of Ca(AlH₄)₂ with the simulated powder pattern⁷ using the refined lattice parameters of the experimental data reveals a good fit between both patterns (Figure S1 in the Supporting Information). The phase purity of the alanate sample is confirmed. CaAlH₅ was obtained, together with Al, from the alanate sample after thermolysis at 180 °C. The simulated pattern using the calculated structure data matches with the measured powder pattern (Figure S2 in the Supporting Information). The Rietveld plot after the final run is shown in Figure 1. (The crystallographic data are summarized in Table S1 in

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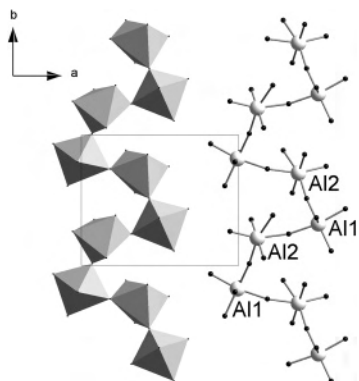


Figure 2. Plot of the crystal structure of CaAlH_5 showing the helical arrangement of $[\text{AlH}_6]$ along the b axis.

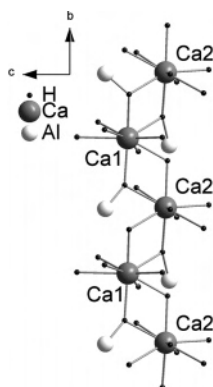


Figure 3. Plot of the crystal structure of CaAlH_5 showing the coordination of the Ca atoms by nine H atoms.

the Supporting Information. Starting and refined parameters are summarized in Table S2 in the Supporting Information.)

At an early stage of the study, similarity between the crystal structures of CaAlH_5 and BaAlH_5 was expected but a comparison of the powder patterns showed very soon that the crystal structures had to be different. The crystal structure of CaAlH_5 , isotopic to α' - SrAlF_5 ¹⁶ and α' - BaFeF_5 ,¹⁷ consists of corner-sharing $[\text{AlH}_6]$ octahedra that form helical chains along the b axis (Figure 2). The two crystallographically independent Al atoms alternate within the chains. The helical arrangement is different from the zigzag chains of $[\text{AlH}_6]$ octahedra in the crystal structure of BaAlH_5 .¹⁸ Each of the Ca atoms of the CaAlH_5 structure is coordinated by nine H atoms with a distance between 2.3 and 2.6 Å and another H atom with a bond length of more than 3 Å (Figure 3). The ground-state energies of $\text{Ca}(\text{AlH}_4)_2$, CaH_2 , solid Al, and gas-phase H_2 were calculated in a manner similar to that described above for CaAlH_5 . The starting structures were taken to be those published by Løvrvik⁷ for $\text{Ca}(\text{AlH}_4)_2$ and Wyckoff²³ for CaH_2 . The relaxed $\text{Ca}(\text{AlH}_4)_2$ structure had lattice constants of $a = 13.403$ Å, $b = 9.506$ Å, and $c =$

Table 2. Calculated Reaction Energies for Calcium Alanate Dehydrogenation Reactions (kJ/mol)

reaction	ΔE
$\text{Ca}(\text{AlH}_4)_2 \rightarrow \text{CaAlH}_5 + \text{Al} + 1.5\text{H}_2$	-7.23
$\text{CaAlH}_5 \rightarrow \text{CaH}_2 + \text{Al} + 1.5\text{H}_2$	59.78
$\text{Ca}(\text{AlH}_4)_2 \rightarrow \text{CaH}_2 + 2\text{Al} + 3\text{H}_2$	52.55

9.032 Å, slightly larger than those of Løvrvik,⁷ making them closer to the experimentally determined values. The optimized atomic coordinates were in good agreement with those previously published.⁷ The optimized CaH_2 structure had lattice constants $a = 5.352$ Å, $b = 3.811$ Å, and $c = 6.584$ Å, with the coordinates of the atoms (all site 4c) of (0.2497, $1/4$, 0.0825) for Ca and (0.2502, $1/4$, 0.4162) and (0.0000, $1/4$, 0.7497) for the two H atoms, fully specifying the $Pnma$ (No. 62) structure. Likewise, the optimized lattice constant for Al was 4.047 Å and the H_2 bond length was 0.749 Å. Combining the calculated energies yielded the reaction energies listed in Table 2. Note that the reaction energies listed in Table 2 are different in potential energy only. It must be expected that the calculated reaction enthalpy, including zero-point energy corrections, would be less than the values presented here without any zero-point energy contribution.^{24,25} The calculated reaction energy for the first dehydrogenation step indicates that this reaction is indeed exothermic and unsuitable for reversible H_2 storage. On the other hand, the dehydrogenation energy of CaAlH_5 (39.9 kJ/mol of H_2 without zero-point energy corrections) lies within the target range for H_2 storage materials.²⁶

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Note Added after ASAP Publication. This article was released ASAP on April 14, 2006, with an incorrect spelling of isotopic on the second page. The correct version was posted on April 27, 2006.

Supporting Information Available: Experimental part and description of the structural refinement of CaAlH_5 and tables listing calculated and refined atomic coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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