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Double-Bridge Bonding of Aluminium and Hydrogen in the Crystal Structure of γ -AlH₃

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Aluminum trihydride (alane) is one of the most promising among the prospective solid hydrogen-storage materials, with a high gravimetric and volumetric density of hydrogen. In the present work, the alane, crystallizing in the γ -AlH₃ polymorphic modification, was synthesized and then structurally characterized by means of synchrotron X-ray powder diffraction. This study revealed that γ -AlH₃ crystallizes with an orthorhombic unit cell (space group *Pnmm*, $a = 5.3806(1)$ Å, $b = 7.3555(2)$ Å, $c = 5.77509(5)$ Å). The crystal structure of γ -AlH₃ contains two types of AlH₆ octahedra as the building blocks. The Al–H bond distances in the structure vary in the range of 1.66–1.79 Å. A prominent feature of the crystal structure is the formation of the bifurcated *double-bridge* bonds, Al–2H–Al, in addition to the normal bridge bonds, Al–H–Al. This former feature has not been previously reported for Al-containing hydrides so far. The geometry of the double-bridge bond shows formation of short Al–Al (2.606 Å) and Al–H (1.68–1.70 Å) bonds compared to the Al–Al distances in Al metal (2.86 Å) and Al–H distances for Al atoms involved in the formation of normal bridge bonds (1.769–1.784 Å). The crystal structure of γ -AlH₃ contains large cavities between the AlH₆ octahedra. As a consequence, the density is 11% less than for α -AlH₃.

Introduction

Aluminum trihydride (alane), having a high gravimetric (10 wt %) and volumetric density of hydrogen (twice that of liquid H₂), is among the most promising materials for on-board hydrogen-storage applications.

An ethereal complex of solvated alane was first synthesized in 1947 by an exchange reaction between AlCl₃ and lithium hydride in ether solution.¹ Its synthesis in nonsolvated form was first described in ref 2. AlH₃ forms six polymorphic modifications, α , α' , β , γ , δ , and ϵ , which are considered to be polymers (AlH₃)_{*n*}.² The measured thermodynamic properties of alane show that the equilibrium hydrogen pressure in

the Al–AlH₃ system is extremely high at ambient temperatures exceeding 25 kBar; therefore, alane should easily decompose at normal conditions and can be only formed by application of extremely high hydrogen pressures.^{3,4} However, AlH₃ does not release very much hydrogen even while storing for years because the decomposition is kinetically hindered, possibly because of the formation of a thin protective oxide layer.

At atmospheric pressure, AlH₃ desorbs hydrogen at rather moderate temperatures (350–400 K, depending on its preparation history). Sufficiently rapid and controllable decomposition of AlH₃ and efficient synthesis routes to make the Al–AlH₃ system reversible are focuses in ongoing research (see, for example, ref 5). The doping of alane with LiH assists in solving the first task. All other alane modifications, including γ -alane, are less stable than α -alane

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(1) Finholt, A. E.; Bond, C., Jr.; Schlesinger, H. I. *J. Amer. Chem. Soc.* **1947**, *69*, 1199–1203.

(2) Brower, F. M.; Matzek, N. E.; Reigler, P. F.; Rinn, H. W.; Roberts, C. B.; Schmidt, D. L.; Snover, J. A.; Terada, K. *J. Amer. Chem. Soc.* **1976**, *98*, 2450–2453.

(3) (a) Tkacz, M.; Filipek, S.; Baranowski, B. *Pol. J. Chem.* **1983**, *57*, 651–653. (b) Baranowski, B.; Tkacz, M. *Z. Phys. Chem.* **1983**, *135*, 27.

(4) Kononov, S. K.; Bulychev, B. M. *Inorg. Chem.* **1995**, *34*, 172.

(5) Sandroock, G.; Reilly, J. J.; Graetz, J.; Zhou, W.-M.; Johnson, J.; Wegrzyn, J. *Appl. Phys. A* **2005**, *80*, 687–690.

and transform into the α -modification at temperatures slightly above ambient.⁶

α -AlH₃ is the best-studied modification of alane. These studies included its structural characterization.^{7,8} The high-resolution synchrotron X-ray diffraction (SR-XRD) structural study⁸ showed that a rhombohedral lattice of α -AlH₃ (space group $R\bar{3}c$, $a = 4.44994(5)$ Å, $c = 11.8200(2)$ Å, $V = 202.701(4)$ Å³) is composed of vertex-sharing AlH₆ octahedra. The Al–H–Al bridge bonds are formed and have the following characteristics: $\angle\text{Al–H–Al} = 142.0(7)^\circ$, $d_{\text{Al–H}} = 1.712(3)$ Å. The refinements of the diffraction data indicated a small charge transfer from Al to H, corresponding to the formation of Al^{+0.15} and H^{−0.05}.

However, the structures of the other allotropic modifications of the alane have not been reported yet. The present paper gives results of the studies of the crystal structure of γ -AlH₃ by means of SR-XRD.

Experimental Section

Synthesis of γ -alane was performed by two different groups, the Institute of Nanotechnology, FZK, in Germany (M.F. and C.F.) and Moscow State University in Russia (B.M.B.). Both synthesis techniques, despite differences in the synthesis processes, resulted in obtaining a nearly single-phase γ -AlH₃. For further studies, by SR-XRD, the sample prepared at FZK was used. However, both synthesis routes will be described below.

Synthesis at Institute of Nanotechnology, FZK. Reagents. Diethyl ether (Merck, certified ACS, 99% purity) was double-distilled over sodium/benzophenone and LiAlH₄ and stored under purified nitrogen. AlCl₃ (Merck, anhydrous, >98%) was used as received. LiAlH₄ (Merck, >97%) was purified prior to use by dissolution in DEE and filtration of a light gray residue. After the solvent was evaporated under a vacuum, a white powder was obtained. According to powder XRD measurements, the material was purely a single phase.

Chemical synthesis of γ -AlH₃ was carried out on the bench using Schlenk tube techniques. The glassware was evacuated down to a pressure of 10^{−3} mbar and flushed with dry oxygen-free nitrogen prior to use. Solids were handled in an argon-filled glove box equipped with a recirculation and regeneration system. Both the water and oxygen concentrations were kept below 1 ppm during operation. The synthesis procedure is a modification of a description given in the literature.¹

Diethyl ether solutions of LiAlH₄ (2.4 g, 250 mL of Et₂O) and AlCl₃ (2.1 g, 70 mL of Et₂O) were prepared; both were precooled in an ice bath, and the AlCl₃ solution was quickly added to the LiAlH₄ solution with stirring. The reaction proceeded immediately, forming a fine, white precipitate. Stirring was continued for a period of 5 min; the precipitate was allowed to settle, and the solution was filtered through a fine grade glass filter frit into a round-bottom flask fitted with a nitrogen inlet. After filtration, the solvent was slowly removed at room temperature under vacuum (10^{−3} mbar), and the remaining white residue was ground and heated under vacuum at 60 °C in a rotating glass oven (Büchi B585) for 4 h.

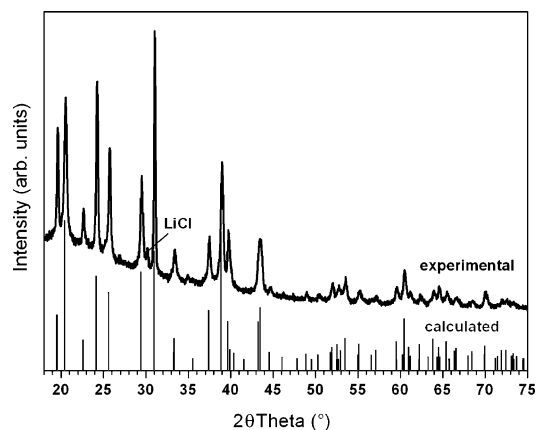


Figure 1. Experimental and calculated powder XRD pattern of γ -AlH₃ (Cu K α). The calculation was performed on the basis of the structural data of this paper.

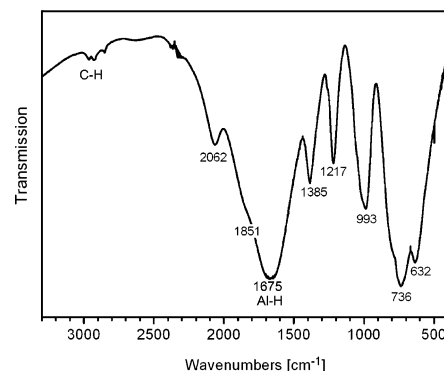


Figure 2. IR spectrum of γ -AlH₃.

The solid was finally transferred to a fine-grade glass filter frit, washed several times with small aliquots of Et₂O to remove excess LiAlH₄ and any remaining AlH₃-etherate, and dried under vacuum, yielding 1.5 g (75%) of aluminum hydride.

The material was a nearly pure single phase. The X-ray powder pattern resembled the reference pattern ICDD-PDF #38-0757 for γ -AlH₃ with only a trace amount of LiCl in the material (see Figure 1). The infrared spectra of the samples showed a broad band with a maximum at 1675 cm^{−1} in the Al–H stretch region, and only a residual amount of hydrocarbons was detected in the C–H stretch region at 3000 cm^{−1}, see Figure 2.

Instrumentation and Analyses. Solid-state infrared spectra of the product (as KBr pellets) were recorded in the range of 4000–370 cm^{−1} under a nitrogen atmosphere and ambient conditions by using a Perkin-Elmer Spectrum GX FTIR spectrometer. The evaluation was done with the Perkin-Elmer Spectrum, version 2.00, Software.

Powder X-ray diffraction patterns were obtained with a Philips X'PERT diffractometer (Cu K α radiation, 2 kW, with X'Celerator RTMS detector, automatic divergence slit). The powder was measured on a single Si crystal and sealed in the glove box by an airtight hood made of Kapton foil, the foil being mounted out of the focus of the diffractometer. The software for data acquisition and evaluation was X'PERT HighScore 2.2.

Synthesis at Moscow State University. Commercial LiAlH₄ was purified by recrystallization from the ether–toluene solution to a purity of 99.3% (these data were obtained by quantitative element analysis, chromatography of the gaseous phase, IR spectroscopy, and XRD). Commercial AlCl₃ was additionally purified by sublimation in a glass ampule above aluminum metal to a purity of

(6) (a) Graetz, J.; Reilly, J. J. *J. Alloys Compd.* **2006**, *424* (1–2), 262–265. (b) Graetz, J.; Reilly, J. J. *J. Phys. Chem. B* **2005**, *109*, 22181–22185.

(7) Turley, J. W.; Rinn, H. W. *Inorg. Chem.* **1969**, *8*, 18–22.

(8) Maehlen, J. P.; Yartys, V. A. In *Advanced Materials for Energy Conversion III*; Chandra, D., Petrovic, J., Bautista, R. G., Imam, A., Eds.; The Minerals, Metals & Materials Society: Warrendale, PA, 2006; pp 77–85.

99.9%. Total content of the transition metals in both initial chemicals was less than $10^{-3}\%$. Ether and benzene were purified by boiling and distillation over LiAlH₄.

γ -AlH₃ was synthesized according to the technique described in ref 1 using the reaction $3\text{LiAlH}_4 + \text{AlCl}_3 \rightarrow 4\text{AlH}_3 + 3\text{LiCl}$ in ether–benzene solution at room temperature. A 12% excess of lithium alanate was used, compared to the stoichiometry. After the reaction was complete, the solution was heated for a distillation of the mixed solvent until the hydride started to crystallize at 75–76 °C. The residual suspension was cooled under Ar gas. Solid γ -AlH₃ was received as thin needles or plates with sizes of $(1\text{--}2) \times (3\text{--}5) \times (20\text{--}30) \mu\text{m}$. This product was separated, washed by ether, and dried in a vacuum under slight heating.

Synchrotron X-ray Diffraction. SR-XRD studies of γ -alane were performed at the Swiss-Norwegian Beam Line (SNBL, BM1) at the European Synchrotron Radiation Facility (Grenoble). The high-resolution powder diffraction data for γ -AlH₃ was collected at room temperature with the powder diffractometer (in Debye–Scherrer mode) in steps of 0.003° in the 2θ range from 4.020 to 50.001° . Monochromatic X-rays were obtained from a channel-cut Si (111) crystal. For the measurements, the sample was put into a 0.7 mm quartz capillary. The wavelength, λ , selected for the measurements was accurately determined to be $\lambda = 0.60008(2) \text{ \AA}$ from separate calibration measurements of a standard LaB₆ sample. The Rietveld analysis of the data was carried out using the GSAS software.⁹

Results and Discussion

The SR-XRD pattern was indexed as an orthorhombic cell with unit cell parameters of $a = 5.3806(1) \text{ \AA}$, $b = 7.3555(2) \text{ \AA}$, $c = 5.77509(5) \text{ \AA}$, and volume, $V = 228.561(7) \text{ \AA}^3$. The use of the rhombohedral α -AlH₃ (space group $R\bar{3}c$ (No. 167) ($a = 4.44994(5) \text{ \AA}$, $c = 11.8200(2) \text{ \AA}$, $V = 202.701 \text{ \AA}^3$) with $33.78 \text{ \AA}^3/\text{fu}$ of AlH₃⁸ for comparison leads to a proposal that the unit cell of γ -AlH₃ contains 6 fu of AlH₃, yielding a higher value of the molecular volume for γ -AlH₃ ($38.10 \text{ \AA}^3/\text{AlH}_3$) and a smaller value, by 11%, of the density of γ -AlH₃ (1.31 g/cm^3), compared to that of α -AlH₃ (1.48 g/cm^3).

Analysis of the powder diffraction pattern showed that the experimentally observed hkl indices obey the following extinction rules: $0kl$, $k + l = 2n$; $h0l$, $h + l = 2n$; $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$. The latter are consistent with the space group $Pnmm$ (No. 58). The FOX software package¹⁰ has been used for this space group to determine the structure of the aluminum sublattice. The calculations yielded the positions of Al atoms occupying 2 different sites: 2-fold $2b$ ($0,0,1/2$) and 4-fold $4g$ ($x,y,0$; $x \approx 0.78$, $y \approx 0.08$). Even without the location of the hydrogen atoms, the refinement, based on the introduction of 6 Al atoms per unit cell, resulted in a rather good fit: $R_p = 5.41\%$, $R_{wp} = 6.91\%$, and $\chi^2 = 2.63$.

Anisotropic line broadening of the diffraction pattern was observed and was accounted for in the refinements using the Thompson–Cox–Hastings pseudo-Voigt-type function

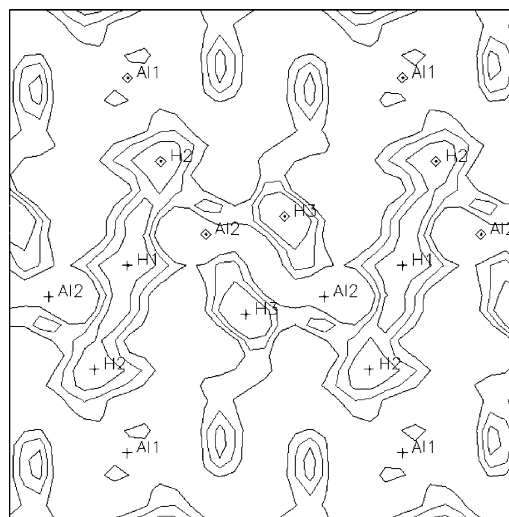


Figure 3. Difference Fourier map plotted in the x,y plane centered at $x,y,z = (1/2, 1/2, 1/2)$ for γ -AlH₃ showing peaks of electron density associated with the H1, H2, and H3 atoms in the vicinity of Al1 and Al2 (the width of the plot is 10 \AA).

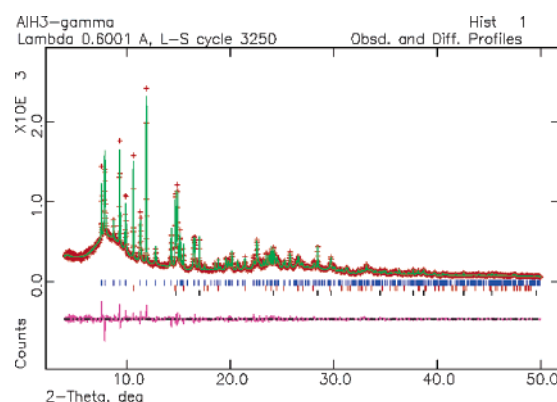


Figure 4. Observed (+), calculated (upper line), and difference (lower line) XRD profiles for γ -AlH₃. Positions of the peaks of the constituent phases are marked (from top to bottom): γ -AlH₃ (83.1(1) wt %), α -AlH₃ (10.7(1) wt %), and Al (6.2(1) wt %). The secondary phases, α -AlH₃ and Al, are formed during storage of the initial phase-pure γ -AlH₃ prior to the SR-XRD measurements.

as proposed in ref 11. Size broadening coefficients, P and X (describing the Gaussian and Lorentzian contributions, respectively), the mixing coefficient, η , and six microstrain parameters for the orthorhombic system were refined. The values of U , V , and W , defining instrumental parameters of the measurements, obtained from refinements of a LaB₆ standard, were fixed.

An interesting feature of the Al sublattice is the formation of very short Al–Al distances of 2.606 \AA between atoms Al2 and Al2. This feature will be further explained later in the paper, after description of the findings, associated with the most important features of the hydrogen sublattice and Al–H bonding in the structure.

Hydrogen atoms in the structure were located from the difference Fourier synthesis maps allowing identification of 4 different crystallographic sites occupied by 18 H atoms/unit cell. These included H1 ($2d$ $0, 1/2, 1/2$), H2 ($4g$ $x, y, 0$), H3 ($4g$ $x, y, 0$), and H4 ($8h$ $x, y, 0$). Figure 3 shows a

(9) Larson, A. C.; van Dreele, R. B. General Structure Analysis System (GSAS), LANSCE, MS-H 805 (1994).

(10) Favre-Nicolin, V.; Cerný, R. *J. Appl. Crystallogr.* **2002**, *35*, 734–743.

(11) Stephens, P. J. *Appl. Crystallogr.* **1999**, *32*, 281–289.

Table 1. Experimental Details and Crystallographic Data for γ -AlH₃

composition	AlH ₃
fw	30.006
cryst syst	orthorhombic
space group	<i>Pnnm</i> (No. 58)
<i>a</i> (Å)	5.3806(1)
<i>b</i> (Å)	7.3555(2)
<i>c</i> (Å)	5.77509(5)
<i>V</i> (Å ³)	228.561(7)
<i>Z</i>	6
<i>D</i> (g cm ⁻³)	1.308
color	white
temp (K)	293
wavelength (Å)	0.60008
diffractometer	Beamline BM01, SNBL, ESRF, France
data collection mode	Debye–Scherrer
2 θ (deg)	4.020–50.001, increments of 0.003
no. of points	15 327
refinement	
<i>R</i> factors and GOF	<i>R</i> _{wp} = 0.0614, <i>R</i> _p = 0.0488, and χ^2 = 2.079

Table 2. Atomic Coordinates and Thermal Parameters for γ -AlH₃

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (×100 Å ²)
Al1	2 <i>b</i>	0	0	1/2	1.27(5)
Al2	4 <i>g</i>	0.7875(2)	0.0849(2)	0	0.40(2)
H1	2 <i>d</i>	0	1/2	1/2	2.0(–)
H2	4 <i>g</i>	0.626(4)	0.278(2)	0	2.0(–)
H3	4 <i>g</i>	0.094(2)	0.130(2)	0	2.0(–)
H4	8 <i>h</i>	0.762(2)	0.078(2)	0.309(1)	2.0(–)

difference Fourier map in which the H1, H2, and H3 atoms are clearly seen in the neighborhood of the Al1 and Al2 atoms.

The introduction of hydrogen atoms into the calculations allowed further improvement of the refinement fits. The *R* values decreased to *R*_p = 4.88%, *R*_{wp} = 6.14%, and χ^2 = 2.08. The good quality of the fit of the powder diffraction data is shown in Figure 4. Table 1 summarizes crystallographic data for γ -AlH₃, and Table 2 gives the atomic coordinates and thermal parameters for γ -AlH₃.

In γ -AlH₃, hydrogen atoms form octahedra around Al. Al1 is bonded with two H2 atoms and four H4 atoms, while Al2 is surrounded by H1, H2, two H3, and two H4 atoms (see Figure 5). The Al–H bonding distances in the structure are in the range of 1.66–1.79 Å (Table 3). Despite the rather large variation, they are all close to the only available Al–H binding distance in α -AlH₃ of 1.712 Å.⁸

The structure of γ -AlH₃ is composed of AlH₆ octahedra, as the building blocks (Figure 6), similar to α -AlH₃. However, these octahedra are connected differently, resulting in formation of hydrogen bridge bonds, Al–H–Al, in α -AlH₃ (Al–H = 1.712 Å, Al–Al = 3.24 Å, \angle 142°) or two different types of bridges in γ -AlH₃ (Figure 5), where AlH₆ octahedra of two kinds share vertices and edges. In addition to a normal bridge bond (γ Al–H = 1.65–1.80 Å, Al–Al = 3.17 Å, \angle 124.9°), a bifurcated bridge bond between two aluminum and two hydrogen atoms is formed. The geometry of this bond (Al–H = 1.68 and 1.70 Å, \angle 100.7°) allows for a close proximity between aluminum atoms Al–Al = 2.606 Å. This appears to be even shorter than the Al–Al distances in Al metal (2.86 Å).

The formation of the bifurcated double-bridge bond, Al–2H–Al, is a prominent feature of the crystal structure of

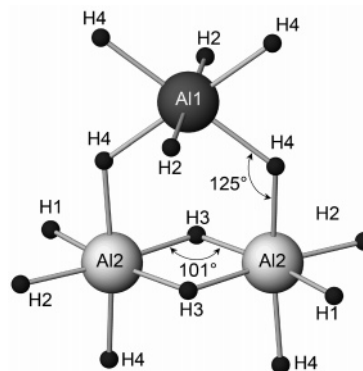


Figure 5. Two types of the available AlH₆ octahedra, Al1H₂H₄ and Al2H1H2H3H4, and their interconnection in the crystal structure of γ -AlH₃. A double-bridge bond, Al2–2H3–Al2, and one type of the bridge bond Al1–H4–Al1 are shown. For Al1, all Al–H distances are large (1.78–1.79 Å). For Al2, the axial bonds, Al–H = 1.78 Å, are as long as the Al1–H distances. However, H atoms participating in the double-bridge bonds, H–2Al–H, form much shorter bonds with Al (1.68 and 1.72 Å). This proximity results in a short interatomic distance between two Al2 atoms of only 2.606 Å and a much lower bond angle (101°) than the normal bridge bond angle of 125°.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) in the Crystal Structure of γ -AlH₃^a

atoms	distances	atoms	distances	atoms	angles
Al1–4Al2	3.1679(4)	Al2–H1	1.668(1)	Al1–H4–Al2	124.9(6)
Al1–4H4	1.784(6)	Al2–H2	1.664(8)	Al1–H2–Al2	171.0(2)
Al1–2H2	1.769(8)	Al2–H3	1.68(1)	Al2–H1–Al2	180.0(–)
Al2–2Al1	3.1679(4)	Al2–H3	1.70(1)	Al2–H3–Al2	100.7(7)
Al2–Al2	2.606(2)	Al2–2H4	1.790(8)		

^a All H–H distances in the structure exceed 2.1 Å.

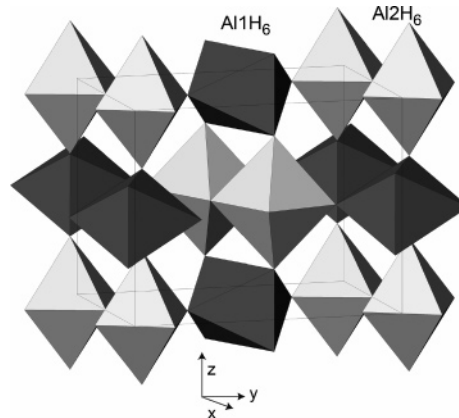


Figure 6. Framework of the AlH₆ octahedra in the crystal structure of γ -AlH₃ showing interconnection between two types of the available AlH₆ units, Al1H₆ and Al2H₆. Octahedra are connected by vertices (Al1H₆–Al2H₆) or by edges (Al2H₆–Al2H₆). This results in the formation of normal bridge bonds, H–Al–H, or double-bridge bonds, Al–2H–Al (latter).

γ -AlH₃. This feature is unique for the Al-containing hydrides and has not been previously reported for its hydrides.

Indeed, the AlH₆ octahedra are frequently found in the crystal structures of Al-containing hydrides. They exist either as AlH₆^{3–} ions or as covalently bound neutral AlH₆ polyhedra. The AlH₆^{3–} ions are present as isolated units in the structures of the R₃AlH₆ hexahydrides, for example, in Na₃–AlH₆,¹² K₂LiAlH₆, and K₂NaAlH₆.¹³

(12) Ronnebro, E.; Noreus, D.; Kadir, K.; Reiser, A.; Bogdanovic, B. *J. Alloys Compd.* **2000**, 299, 101–106.

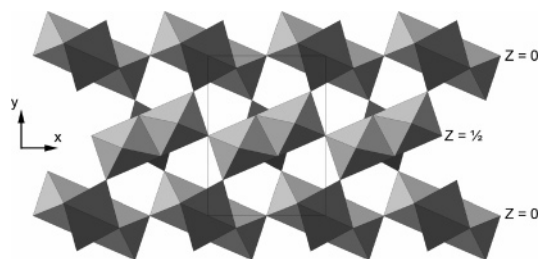


Figure 7. Projection of the crystal structure of $\gamma\text{-AlH}_3$ along [001] shown as a packing of the AlH_6 octahedra. Large cavities in the structure are clearly seen.

On the other hand, AlH_6 octahedra share vertices in the crystal structure of $\alpha\text{-AlH}_3$,⁸ thus, forming normal bridge bonds, Al-H-Al . Such bonds are a consequence of the electron deficiency of the elements of the third group, which may self-stabilize by the formation of 3-center 2-electron bridge bonds in the case of covalent compounds.

Finally, one additional feature of the crystal structure of $\gamma\text{-AlH}_3$ should be mentioned. This feature lies in the formation of large cavities between the AlH_6 octahedra. The cavities are clearly seen in the Figure 7. The vertices of a set of two edge-connected Al_2H_6 octahedra are always connected to two other pairs of edge-connected Al_2H_6 octahedra and to four single vertex-connected AlH_6 octahedra. Hence, the strands of Al_2H_6 are always separated by single AlH_6 octahedra, which are differently oriented in space. As a result of such packing, the structure of $\gamma\text{-AlH}_3$ has a much smaller, by 11%, density than $\alpha\text{-AlH}_3$.

The decomposition reaction enthalpy of $\gamma\text{-AlH}_3$ is 7.1 kJ/mol,⁶ which is small, compared to that one of $\alpha\text{-AlH}_3$ which is 11.4 kJ/mol.⁶ In the case of AlH_3 , the reaction enthalpy is the same as the enthalpy of formation because the products are elements; therefore, the average binding energy in $\gamma\text{-AlH}_3$ is lower than that in $\alpha\text{-AlH}_3$. Since the (thermodynamic) decomposition temperature and the equilibrium pressure is related to the Gibbs free energy, this should make a contribution to lower the decomposition temperature of the γ -modification. A different contribution comes from the reaction entropy, which should be lower in the case of the γ -compound, if the assumption of a higher degree of disorder in the γ -phase is justified. At equilibrium ($\Delta G = 0$), the Gibbs equation can be written as

$$T_{\text{eq}} = \frac{\Delta H}{\Delta S} \quad (1)$$

Thus, both the numerator and denominator decrease in eq 1 when changing from the α - to γ -phase. However, because the equilibrium pressure of the $\gamma\text{-AlH}_3$ is higher and the decomposition temperature is lower, this indicates a dominating effect of the average binding energy, ΔH , over the entropy.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0617487

(13) Graetz, J.; Lee, Y.; Reilly, J. J.; Park, S.; Vogt, T. Structures and thermodynamics of the mixed alkali alanate. *Phys. Rev. B*, **2005**, *71*, 184115.