The crystal structure of γ-AlD₃

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Abstract

γ-AlD₃ was synthesized from LiAlD₄ and AlCl₃ via thermal decomposition of aluminum hydride etherate in presence of excess LiAlD₄. γ-AlD₃ was determined by powder neutron diffraction and synchrotron X-ray diffraction to crystallize in the space group *Pnnm*. The orthorhombic structure has unit-cell dimensions $a = 7.3360(3)$ Å, $b = 5.3672(2)$ Å and $c = 5.7562(1)$ Å, and it consists of both corner- and edge-sharing AlD₆ octahedra where each hydrogen is shared between two octahedra. The average Al–D distances in octahedra with edge-sharing is 1.706 Å and in the octahedra with only corner-sharing 1.719 Å.
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1. Introduction

AlH₃ (alane) is one of the solid compounds with the largest hydrogen content (10.1 wt.%) and as such of interest for hydrogen storage applications. AlH₃ has been found to take at least six different crystal structures depending on the synthesis route [1]: α, α′, β, γ, δ and ε, of which the four former structure modifications have been synthesized reproducibly. α-AlH₃ is the most stable phase [1], but measurements of dehydrogenation enthalpy [2–5] indicate an equilibrium pressure of more than 10^4 bar at room temperature. Nevertheless, α-AlH₃ is kinetically stable and can be stored for several years [6].

The crystal structures of α- [7,8], α′- [8] and β-AlD₃ [9] have previously been determined, and the powder X-ray diffraction (PXD) fingerprint for γ-AlH₃ have been given by Brower et al. [1]. α-, α′- and β-AlD₃ crystallize in structures with 3D networks of corner-sharing AlD₆ octahedra, where each hydrogen atom is shared between two octahedra. The structure modifications differ by the connectivity of the octahedra. For α-AlD₃, the octahedra in the first coordination sphere around an octahedron are not interconnected, whereas for α′-AlD₃ four of the six octahedra are interconnected in pairs. In β-AlD₃, all six octahedra are bound to two of the others. For α′- and β-AlD₃ the connectivity leads to large channels in the structures.

The Al–D distances in α-AlD₃ (1.709 Å Turley et al. [7], 1.711 Å Brinks et al. [8]), α′-AlD₃ (1.71 Å [8]) and β′-AlD₃ (1.712(1) Å [9]) are similar, but shorter than the distances in hexa-alanates like Na₂LiAlD₆ with Al–D distances of 1.760 Å in the isolated AlH₆³⁻ complexes [10].

In the present work, γ-AlD₃ was synthesized by the solid-state method described by Brower et al. [1], where solid aluminum hydride etherate is heated in presence of solid LiAlD₄. γ-AlD₃ of about 80% purity was obtained along with α-AlD₃ and LiCl. The crystal structure was determined by synchrotron-radiation powder X-ray diffraction (SR-PXD) and powder neutron diffraction (PND).

2. Experimental

LiAlD₄ (≥98 wt.% purity) was purchased from Aldrich. AlCl₃ (≥99 wt.% purity) was purchased from Alfa. The LiAlD₄ was purified via Soxhlet extraction.

Diethyl ether (Fischer Scientific, certified ACS, 99.9% purity) solutions of LiAlD₄ and AlCl₃ were prepared. The LiAlD₄ solution was added to the AlCl₃ solution in a 4:1 molar ratio at room temperature and stirred for 2–3 min. LiCl was filtered by a medium grade glass filter and diethyl ether was removed overnight under vacuum at 35 °C. The product was ground to a fine powder and heated at 65 °C for 2 h. The final γ-AlD₃ was obtained by washing with diethyl ether with subsequent drying at room temperature overnight under vacuum.

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PND data at 22 °C were collected with the PUS instrument at the JEEP II reactor at Kjeller (Norway) [11]. Neutrons with $\lambda = 1.5554$ Å were obtained from a Ge(5 1 1) focussing monochromator. The detector unit consists of two banks of seven position-sensitive ^{3}He detectors, each covering 20° in 2θ (binned in steps of 0.05°). The sample was placed in a rotating cylindrical vanadium sample holder with 6 mm diameter.

SR-PXD data at 22 °C were collected at the Swiss–Norwegian beam line (station BM01B) at the European synchrotron radiation facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.8 mm boron–silica–glass capillaries. Intensities were measured in steps of $\Delta(2\theta) = 0.006°$. The wavelength 0.50059 Å was obtained from a channel-cut Si(1 1 1) monochromator.

Rietveld refinements were carried out using the program Fullprof (version 3.2) [12]. The neutron scattering lengths and the X-ray form factors were taken from the Fullprof library. Thompson–Cox–Hastings pseudo-Voigt profile functions were used, and the background was modelled by interpolation between manually chosen points. The instrumental resolution of SR-PXD was found by a LaB$_6$ standard.

3. Results and discussion

Based on the SR-PXD and PND data, γ-AlD$_3$ could be indexed as orthorhombic with unit-cell dimensions of $a = 7.34$ Å, $b = 5.37$ Å and $c = 5.76$ Å. By inspection of single reflection in
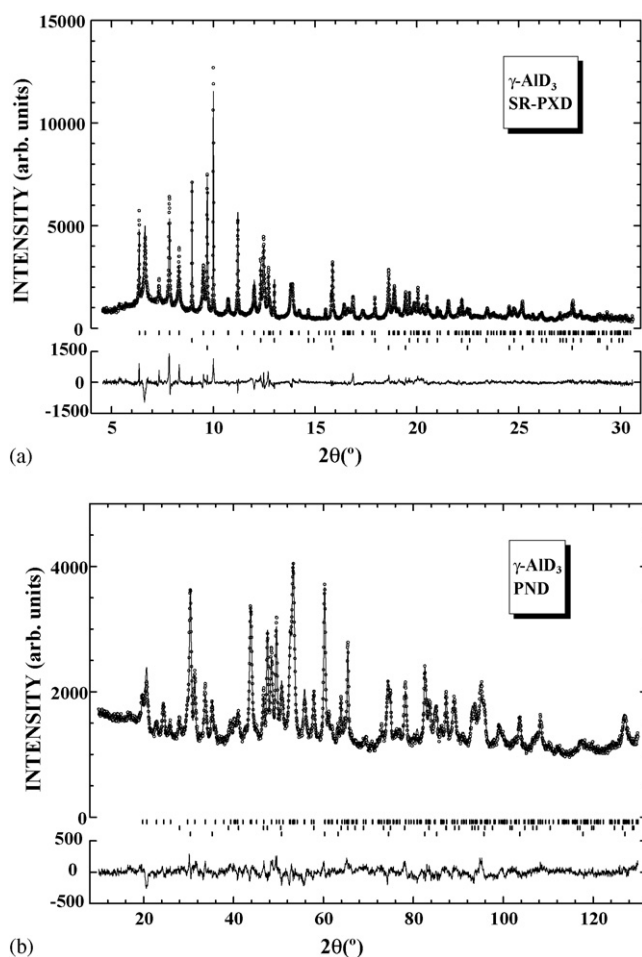

Fig. 1. Observed intensities (circles) and calculated intensities from Rietveld refinements (upper line) of for γ-AlD$_3$ at 22 °C for (a) SR-PXD (BM01B, ESRF) and (b) PND (PUS, Kjeller) data. Positions of Bragg reflections are shown with bars for γ-AlD$_3$, α-AlD$_3$ and LiCl (from top). The difference between observed and calculated intensity are shown with the bottom line.

Table 1
Refined structural parameters for γ-AlD3

Atom	x	y	z	B (Å^2)
Al1	0	0	0	1.29(13)
Al2	0.4174(5)	0.7127(6)	0	0.68(7)
D1	0.2044(9)	0.8269(11)	0	1.20(10)
D2	0.3668(10)	0.3931(13)	0	3.1(2)
D3	0	1/2	1/2	1.8(2)
D4	0.4174(6)	0.7038(8)	0.3009(6)	1.80(8)

The space group is *Pnnm*, $Z = 6$, and the unit-cell dimensions are $a = 7.3360(3)$ Å, $b = 5.3672(2)$ Å and $c = 5.7562(1)$ Å. Reliability factors are $R_{wp} = 8.43\%$ and $\chi^2 = 5.10$ for the SR-PXD data and $R_{wp} = 4.06\%$ and $\chi^2 = 2.46$ for the PND data. Estimated standard deviations in parentheses.

this orthorhombic unit cell it is evident that the width of the reflections are very different in small angle regions. This could be caused either by a lower symmetry than orthorhombic or presence of severe anisotropic broadening. Initial attempts were made to solve the structure in lower symmetries, but by including anisotropic broadening the Rietveld refinements improved. Furthermore, after optimising the anisotropic broadening, the fit of the Rietveld refinement was not deteriorated by going back to orthorhombic symmetry. Hence orthorhombic symmetry was used in the final refinements.

Subsequent to the indexing, the approximate Al positions were determined by the FOX software [13] in space group *P*1 based on the SR-PXD data. Similarly, the D positions were determined by FOX from the PND data with the Al positions fixed. The atomic positions were further optimized with
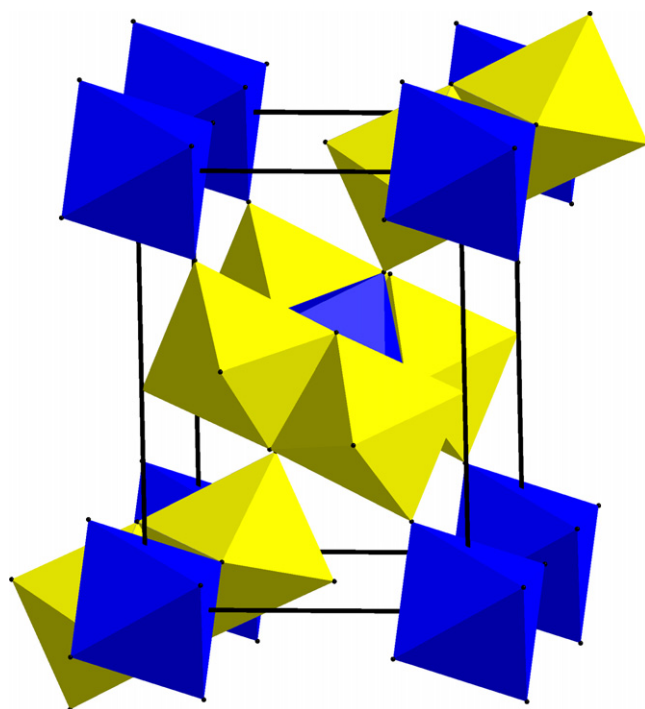

Fig. 2. The atomic arrangement of γ-AlD$_3$ in the unit cell. The two different Al sites are illustrated by different colour of the octahedra. Al1D$_6$ octahedra are blue and Al2D$_6$ octahedra are yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)