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Synthesis and Crystal Structure of Sr_2AlH_7: A New Structural Type of Alkaline Earth Aluminum Hydride

Qing-An Zhang,[†] Yumiko Nakamura,[†] Ken-ich Oikawa,[‡] Takashi Kamiyama,[‡] and Etsuo Akiba*,[†]

*National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5,
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and High-Energy Accelerator Research
Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-080, Japan*

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The title hydride and its deuteride were successfully synthesized. The heavy atom structure and hydrogen positions were determined respectively by X-ray powder diffraction and time-of-flight neutron powder diffraction. They crystallize with a new monoclinic structure in space group *I*2 (No. 5); cell parameters: $a = 12.575(1)$ Å, $b = 9.799(1)$ Å, $c = 7.9911(8)$ Å, $\beta = 100.270(4)°$ (hydride), $a = 12.552(1)$ Å, $b = 9.7826(8)$ Å, $c = 7.9816(7)$ Å, $\beta = 100.286(4)°$ (deuteride), $Z = 8$. Sr_2AlH_7 is the first example that consists of isolated $[AlH_6]$ units and infinite one-dimensional twisted chains of edge-sharing $[HSr_4]$ tetrahedra along the crystallographic *c* axis.

Alanates are potential candidates for hydrogen storage applications because of their high hydrogen content.[1−8] So far, only a few crystal structures of ternary alanates have been reported. For example, the structure of $NaAlH_4$ [9] is made up of tetrahedral $[AlH_4]^-$ anions and Na^+ cations, while the structure of Na_3AlH_6[10] can be described as octahedral $[AlH_6]^{3-}$ anions and Na^+ cations. Recently our interest is to synthesize new alkaline earth metal aluminum hydrides. In the previous work,[11] we found that the Zintl compound $SrAl_2$ can react with hydrogen to form a Zintl hydride $SrAl_2H_2$ under a hydrogen pressure of 5 MPa at about 473 K. The structure of this hydride contains a two-dimensional polymer Zintl anion, in which one H atom is covalently bonded to each Al atom. With increasing hydrogenation temperature, another hydride was found, but its crystal structure and chemical composition were not analyzed. In this paper, we report on the synthesis and crystal structure of the new alkaline earth metal aluminum hydride, namely, Sr_2AlH_7, which was formed by hydrogenation of $SrAl_2$ at a higher temperature. This hydride is the first ternary alanate that consists of isolated $[AlH_6]$ units and infinite one-dimensional twisted chains of edge-sharing $[HSr_4]$ tetrahedra. Differentiating from $NaAlH_4$,[9] Sr_2AlH_7 contains not only Al−H bonds forming octahedral $[AlH_6]^{3-}$ anions but also Sr−H bonds forming $[HSr_4]$ tetrahedra. Thus the H/M (where H and M indicate hydrogen and metals, respectively) ratio of Sr_2AlH_7 is more than that of $NaAlH_4$. On the other hand, the existence of $[HSr_4]$ units easily leads to restructuring SrH_2 during decomposition. This feature is significant for improving the dehydriding and rehydriding kinetics because the slow kinetics hinders the practical applications of alanates. Therefore, Sr_2AlH_7 can be considered as a possible candidate for hydrogen storage application.

All steps of synthesis and sample preparation for X-ray and neutron diffraction were carried out under a dry argon atmosphere. $SrAl_2$ alloy was prepared by arc melting of Sr (Furuuchi chemical, 99.9%) and Al (Furuuchi chemical, 99.99%) metals. Before preparation, the loss of Sr during arc melting was determined to be about 3 wt %. On the basis of stoichiometric amounts of starting materials, thus, an extra 3 wt % of Sr was added to compensate the loss of Sr during arc melting. The alloy was remelted four times to ensure homogeneity in the arc melt furnace. The ingot was ground to powders with particle size smaller than 45 μm. The powder samples (∼2 g for preparing hydride and ∼6 g for preparing deuteride) were loaded into stainless steel containers and placed in stainless steel autoclaves. Hydrogenation reaction of $SrAl_2$ was carried out under a hydrogen pressure of 7 MPa

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* Author to whom correspondence should be addressed. E-mail: e.akiba@aist.go.jp. Fax: +81-298-61-4541.

[†] National Institute of Advanced Industrial Science and Technology.

[‡] High-Energy Accelerator Research Organization (KEK).

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at 543 K for 10 days. The deuteride sample was prepared under a deuterium pressure of 7 MPa at 533 K for 15 days. The reaction products were dark gray and sensitive to air. The hydrogen (or deuterium) contents of the samples were measured using a hydrogen determinator LECO RH-402.

X-ray powder diffraction data of the hydride sample were obtained using a Rigaku RINT-2500V diffractometer equipped with a rotating anode generator of Cu Kα under the conditions of 50 kV and 200 mA. The X-ray diffraction pattern showed that the sample contained a new hydride, Al, SrH_2, and a small amount of the unreacted $SrAl_2$. After subtraction of the diffraction peaks of Al, SrH_2, and the unreacted $SrAl_2$, the X-ray pattern was indexed by ITO12[12] to a monoclinic body-centered unit cell, leading to the possible space groups *I*2 (No. 5), *Im* (No. 8), *Ia* (No. 9), *I*2*/m* (No. 12) and *I*2*/a* (No. 15). The integrated intensities of the new hydride phase were extracted from the XRD pattern by the Le Bail refinement using RIETAN-2000.[13] All attempts to solve the structure in the possible space groups and with the possible contents of Sr and Al were made with the EXPO program.[14,15] As a result, only that in space group *I*2 (No. 5) and with the content of Sr_2Al ($Z = 8$) was successful. In this structure, however, the origin was freely floating along the *b* axis. During moving the origin along the *b* axis, a new symmetry relationship between two Sr atoms or two Al atoms, M (x, y, z) and M′ ($-x$, $-y$, $^1/_2 - z$), was found, which is different from any higher symmetric space group *I*2*/m* (No. 12) or *I*2*/a* (No. 15). Therefore, the origin was fixed by using these constrained coordinates during the subsequent Rietveld refinement with RIETAN-2000.[13] The refined cell parameters of the hydride were $a = 12.575(1)$ Å, $b = 9.799(1)$ Å, $c = 7.9911(8)$ Å, $\boldsymbol{\beta} = 100.270(4)°$, and $V = 968.9(2)$ Å^3 ($R_{wp} = 5.98\%$, $R_p = 4.39\%$, $R_I = 0.97\%$, and $S = 2.23$). The calculated result from the abundance of the hydride and the hydrogen content of the sample showed that the composition of the hydride was Sr_2AlH_7.

Neutron powder diffraction data of the deuteride sample were collected at room temperature using a backward bank of a time-of-flight (TOF) diffractometer Vega[16] at the Neutron Science Laboratory of the High Energy Accelerator Research Organization of Japan. The diffraction data were analyzed by a Rietveld refinement program, RIETAN-2001T.[17] During the refinement, the Sr and Al atom coordinates of the new deuteride were fixed as those refined from the X-ray data of the deuteride sample. The deuterium positions were located by placing the atoms in the octahedral and tetrahedral holes formed by Sr and Al atoms. The occupation factors of the deuterium positions were fixed at unity because they were close to 1 (the differences were smaller than $3\boldsymbol{\sigma}$) during the refinement. The refined cell parameters of Sr_2AlD_7 were $a = 12.552(1)$ Å, $b = 9.7826(8)$ Å, $c = 7.9816(7)$ Å, $\boldsymbol{\beta} = 100.286(4)°$, and $V = 964.3(1)$ Å^3 ($R_{wp} = 2.72\%$, $R_p = 2.15\%$, $R_I = 5.33\%$, and $S = 2.28$). Figure 1 shows the observed and calculated neutron powder diffraction patterns of the deuteride sample. The refined pattern fits the observed data points very well. From the parameters refined by the Rietveld analysis, the phase abundance of Sr_2AlD_7, SrD_2, Al, and $SrAl_2$ were determined to be 50, 14, 35, and 1 wt %, respectively. Thus the deuterium content of the sample can be calculated as 1.99 wt %, which is in good agreement with the measured value 2.07 wt % by the volumetric method.

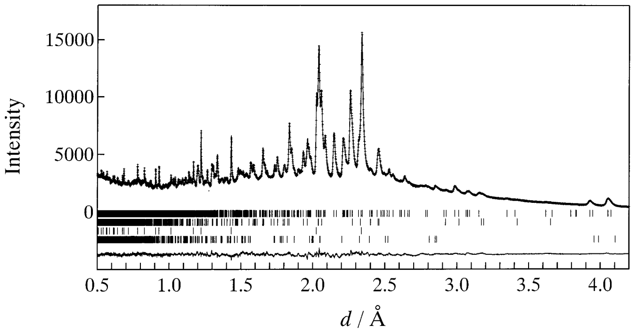

Figure 1. Observed and calculated neutron powder diffraction patterns of Sr_2AlD_7. Reflection markers are for Sr_2AlD_7, SrD_2, Al, and $SrAl_2$ (from above), respectively.

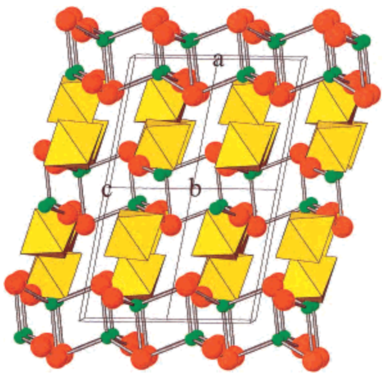

Figure 2. Crystal structure of the Sr_2AlD_7 viewed approximately along the *b* axis (*a* is vertical). The Sr and D atoms forming the one-dimensional twisted chains are respectively represented as larger and smaller spheres, and the isolated $[AlD_6]$ octahedra are centered by Al.

The crystal structure of Sr_2AlD_7 (Figure 2) is built up from isolated $[AlD_6]$ units and infinite one-dimensional chains of edge-sharing $[DSr_4]$ tetrahedra. In the Al-centered $[AlD_6]$ octahedron, the Al−D bond lengths ranging from 1.71 to 1.76 Å (as listed in Table 1) are in good agreement with those in Na_3AlD_6[10] (1.75−1.77 Å). The D-centered $[DSr_4]$ tetrahedra are inverted alternately and share one edge to form infinite one-dimensional twisted chains along the *c* axis. The Sr−D bond lengths (2.46−2.55 Å) compare well with those in binary SrD_2 (2.36−2.80 Å).[18]

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) in Sr_2AlD_7

Sr1(Sr1′)−D3′(D3)	2.45(1)
D7(D7′)	2.46(1)
D5′(D5)	2.53(1)
D4(D4′)	2.54(1)
D6(D6′)	2.58(1)
D1(D1′)	2.59(1)
D2(D2′)	2.63(1)
D6′(D6)	2.65(1)
D1′(D1)	2.72(1)
D6(D6′)	2.72(1)
D2(D2′)	2.83(1)
D4′(D4)	3.37(1)
D4(D4′)	3.51(1)
D2′(D2)	3.79(1)
Sr2(Sr2′)−D5′(D5)	2.41(1)
D3(D3′)	2.43(1)
D1(D1′)	2.47(1)
D7(D7′)	2.53(1)
D7(D7′)	2.53(1)
D7′(D7)	2.55(1)
D4(D4′)	2.64(1)
D2(D2′)	2.70(1)
D5(D5′)	2.76(1)
D3′(D3)	2.84(1)
D2′(D2)	3.26(1)
D4′(D4)	3.66(1)
Al1(Al1′)−D4(D4′)	1.71(1)
D1(D1′)	1.72(1)
D3(D3′)	1.72(1)
D6(D6′)	1.75(1)
D2(D2′)	1.76(1)
D5(D5′)	1.76(1)
D1(D1′)−Al1(Al1′)−D2(D2′)	88.4(4)
D1(D1′)−Al1(Al1′)−D3(D3′)	88.5(3)
D1(D1′)−Al1(Al1′)−D4(D4′)	177.1(4)
D1(D1′)−Al1(Al1′)−D5(D5′)	87.9(3)
D1(D1′)−Al1(Al1′)−D6(D6′)	90.3(3)
D2(D2′)−Al1(Al1′)−D3(D3′)	91.6(4)
D2(D2′)−Al1(Al1′)−D4(D4′)	88.7(4)
D2(D2′)−Al1(Al1′)−D5(D5′)	174.7(3)
D2(D2′)−Al1(Al1′)−D6(D6′)	87.3(4)
D3(D3′)−Al1(Al1′)−D4(D4′)	92.4(4)
D3(D3′)−Al1(Al1′)−D5(D5′)	92.5(3)
D3(D3′)−Al1(Al1′)−D6(D6′)	178.3(3)
D4(D4′)−Al1(Al1′)−D5(D5′)	94.9(4)
D4(D4′)−Al1(Al1′)−D6(D6′)	88.8(3)
D5(D5′)−Al1(Al1′)−D6(D6′)	88.9(3)
D1(D1′)−Al1(Al1′)	1.72(1)
Sr2(Sr2′)	2.47(1)
Sr1(Sr1′)	2.59(1)
Sr1′(Sr1)	2.72(1)
D2(D2′)−Al1(Al1′)	1.76(1)
Sr1(Sr1′)	2.63(1)
Sr2(Sr2′)	2.70(1)
Sr1(Sr1′)	2.83(1)
Sr2′(Sr2)	3.26(1)
Sr1′(Sr1)	3.79(1)
D3(D3′)−Al1(Al1′)	1.72(1)
Sr2(Sr2′)	2.43(1)
Sr1′(Sr1)	2.45(1)
Sr2′(Sr2)	2.84(1)
D4(D4′)−Al1(Al1′)	1.71(1)
Sr1(Sr1′)	2.54(1)
Sr2(Sr2′)	2.64(1)
Sr1′(Sr1)	3.37(1)
Sr1(Sr1′)	3.51(1)
Sr2′(Sr2)	3.66(1)
D5(D5′)−Al1(Al1′)	1.76(1)
Sr2′(Sr2)	2.41(1)
Sr1′(Sr1)	2.53(1)
Sr2(Sr2′)	2.76(1)
D6(D6′)−Al1(Al1′)	1.75(1)
Sr1(Sr1′)	2.58(1)
Sr1′(Sr1)	2.65(1)
Sr1(Sr1′)	2.72(1)
D7(D7′)−Sr1(Sr1′)	2.46(1)
Sr2(Sr2′)	2.53(1)
Sr2(Sr2′)	2.53(1)
Sr2′(Sr2)	2.55(1)
Sr1(Sr1′)−D7(D7′)−Sr2(Sr2′)	108.8(4)
Sr1(Sr1′)−D7(D7′)−Sr2(Sr2′)	116.7(4)
Sr1(Sr1′)−D7(D7′)−Sr2′(Sr2)	104.9(4)
Sr2(Sr2′)−D7(D7′)−Sr2(Sr2′)	104.1(3)
Sr2(Sr2′)−D7(D7′)−Sr2′(Sr2)	110.5(4)
Sr2(Sr2′)−D7(D7′)−Sr2′(Sr2)	111.8(3)

In conclusion, Sr_2AlH_7 is the first example that structurally contains edge-sharing [HSr_4] tetrahedra as well as isolated [AlH_6] octahedra. This finding clearly shows that various crystal structure and metal−hydrogen bonds can exist in alanates. Because of the new arrangement of H atoms, Sr_2AlH_7 has a larger H/M ratio than $NaAlH_4$ and may have better dehydriding kinetics. In order to get more information about this interesting structure, it is necessary to understand whether other isostructural alkaline earth metal aluminum hydrides can exist in Ca−Al−H and Ba−Al−H systems. Thus further investigations are in progress.

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Supporting Information Available: Tables listing detailed atomic coordinates and isotropic thermal displacement parameters for Sr_2AlD_7. This material is available free of charge via the Internet at http://pubs.acs.org.

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